PHOTO-REACTIONS OF ZINC OXIDE

T H E S I S

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by

GARRY WALKER, A.H.-W.C.

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C O N T E N T S

INTRODUCTION

INTRODUCTION

The flaking of paints and tendering of fabrics has led to numerous investigations of the photochemistry of the white pigments involved in their manufacture. The greater part of such work has been concerned with tita-:nium dioxide, investigated initially in paints and fabrics or complex model systems[1,2,3,4,5] and later by Kennedy[6] in simple oxygen-titanium dioxide and nitric oxide-titanium dioxide systems, and McLean[7] in an ammonia-titanium dioxide system.

It has been shown by Kennedy and McLean that oxygen is directly adsorbed as a result of suitable illumina-:tion, and it is believed that such oxygen is utilised during photosorption in the oxidation of certain adsorbed species.

The problem is fundamentally an electronic one in that electrons are made available by illumination and take part in the oxidation reaction. The fundamental conceptions of such a system must, of course be appli-:cable to more than one semiconductor oxide.

Work on zinc oxide has been carried out both in complex and in simpler oxygen-zinc oxide systems, and it is relevant to review here some of the results relating to the interaction of zinc oxide and oxygen.

Photoadsorption of oxygen was observed by Hamilton[8] and/

and Mackenzie[9] on illumination of zinc oxide in oxygen with light of wavelength 3650-4060 A, near the fundamental absorption band. Terenin[10] was the first to observe photodesorption of oxygen when he illuminated oxygen and zinc oxide with an iron-spark. Work by Fujita and Kwan[11] confirmed Terenin's work with a degassed sample (degassed at 300° for several hours) at room temperature and below, using light of wavelength near the fundamental absorption band, but with an oxidised sample (heated in 1 mm. O_2 at 300°) the photoresponse was shown to be irreversible adsorp-:tion. Fujita and Kwan concluded that weakly chemisorbed oxygen molecules are present, showing electronic interaction with the surface of the zinc oxide, and suggested that O_2^- is a probable adsorbed oxygen intermediate. Photoadsorption or -desorption may occur by combining with a positive hole or electron of zinc oxide created by illumination.

The exchange reaction, $^{18}O_2 + {}^{16}O_2 = 2\ {}^{18}O\ {}^{16}O$, was investigated by Winter et al[12] who showed that the exchange reaction was not perceptible below 119°, this supporting the view that oxygen adsorption can occur without dissociation, at least around room tempera-:ture. On the other hand, Melnick[13] has attributed features of the photoconductivity of zinc oxide to the desorption of chemically adsorbed oxygen atoms.

A/

A study of the adsorption of oxygen on zinc oxide at low pressures by Myasnikov[14] has established a quantitative correlation between the adsorption and electroconductivity. Myasnikov proposes a mechanism for the adsorption of oxygen involving the formation of an unstable oxygen compound ($Zn^+ O_2^-$) on the surface having a chemical bond of ionic nature. Evidence is put forward that in photodesorption and photoconductivity the same mechanism of transfer of energy absorbed by the crystal, to the photoactive Zn^+ and $Zn^+ O^-$ centres, pro-:bably excitonic, underlies both processes.

The sensitised formation and decomposition of hydrogen peroxide by zinc oxide is also of interest. When a suspension of zinc oxide in either aerated, distilled water or dilute hydrogen peroxide is illuminated, the same equilibrium concentration of hydrogen peroxide is obtained and the yield of hydrogen peroxide is greatly enhanced by the addition of various oxidisable organic substances. The following mechanisms have been pro-:posed[15,16,17,18,19,20,21].

Thus the formation of hydrogen peroxide is visualised to involve the stages:-

$$ZnO + h\nu \longrightarrow (ZnO)^+ + e$$

$$e + O_2 + H^+ \longrightarrow \cdot HO_2$$

$$2 \cdot HO_2 \longrightarrow H_2O_2 + O_2$$

while in the presence of organic material, e.g. oxalic acid

$$(ZnO)^+ + \tfrac{1}{2} C_2O_4^{2-} \longrightarrow ZnO + CO_2$$

removing/

removing $(ZnO)^+$ to return the catalyst to its original condition, and in the absence of organic material[20]

$$(ZnO)^+ + OH^- \longrightarrow ZnO + \cdot OH$$

$$4 \cdot OH \longrightarrow 2 H_2O + O_2$$

also removing $(ZnO)^+$, but depending on the availability of hydroxyl ions and hence very slow in neutral solu-:tions.

In spite of the views above on adsorption and desorption of oxygen by illumination of zinc oxide, no systematic examination of the kinetics of the actual pressure decrease or increase appears to exist. It was desired to relate such an examination in the first place to that already made known for titanium dioxide, and then if possible to correlate the oxygen so photo-:sorbed with that used in a photosensitised oxidation.

In the present work, investigation has thus been made of the photoadsorption of oxygen on zinc oxide and its dependence on pressure, temperature and illumination, by measuring changes in pressure in a fixed volume system. The effect of illumination on nitric oxide-zinc oxide and ammonia-oxygen-zinc oxide systems has also been studied.

As commercial samples of zinc oxide (analar grade) give a very small uptake of oxygen[3,4], a more active sample was sought for this work. Zinc oxide "hyper-:fine"[22], a very finely divided form of zinc oxide, was prepared/

prepared and was used throughout this work.

As somewhat similar investigations on titanium dioxide have been carried out by Kennedy[6] and McLean[7], it is pertinent to review their results at this point.

PHOTO-REACTIONS OF TITANIUM DIOXIDE

Kennedy[6] found that on illumination of titanium dioxide samples in oxygen, an irreversible adsorption of oxygen took place, the rate of which was for any one sample dependent on oxygen pressure, intensity of illumination and the amount of oxygen adsorbed. He found that plots of change of pressure against time were, in general, initially parabolic and became finally exponential; that the rate of oxygen adsorption was directly proportional to the incident intensity of 3650 Å light and probably to that absorbed; and that the rate of oxygen adsorption was related to the oxygen pressure, by the following equation:-

$$K_1(R.R.) = \frac{K_2\sqrt{P}}{K_2\sqrt{P} + 1}$$ where (R.R.) is the rate

of oxygen uptake at pressure P relative to the rate when P = 50 mm Hg, and K_1 and K_2 are constants; the square root terms indicate a dissociative type of adsorption.

Kennedy found also, that when titanium dioxide was illuminated in nitric oxide a pressure change occurred in accordance with the following equation:-

$$4\,NO \xrightarrow[3650\,Å]{light} N_2O_3 + N_2O$$

(gas) (adsorbed) (gas)

This/

This photoreaction had kinetics similar to the oxygen uptake and occurred independently of some dark reaction with the nitric oxide.

While Kennedy investigated these photo-properties with a number of variously treated titanium dioxide samples, McLean[7] examined a number of reactions using one sample.

McLean studied the photo-sensitised oxidation of adsorbed ammonia, acetone and methyl ethyl ketone on titanium dioxide, and has also re-examined the uptake of oxygen and decomposition of nitric oxide on illuminated titanium dioxide. He has shown that the ratios of the oxygen reacting per g. in the various oxidations have values which are related integrally to the amount of oxygen which can be photoadsorbed and hence to the number of adsorption centres on the titanium dioxide.

The displacement of water from titanium dioxide by ammonia, in the dark, has given some indication of the nature of these centres, the amount of ammonia adsorbed in this way, and the amount of water displaced, also bearing an integer relationship to the number of adsorption sites as indicated by the photoadsorption of oxygen. Stoichiometric relationships between the oxygen used in the oxidations and the products obtained have led to reaction mechanisms for these oxidations being put forward.

The/

The amount of nitric oxide decomposed has also been related to the number of sites present on the sur-:face, and study of the desorption of decomposition products has led to a modification of the decomposition mechanism of Kennedy[6] to

$$3\ NO = N_2O + NO_2^- \text{ (ads.)}.$$

Oxidation of ammonia chemisorbed on the surface of titanium dioxide, under illumination in the presence of gaseous oxygen, and gaseous oxygen ammonia mixture gave similar results, nitrous oxide being found in the gas phase, and nitrite being detected on the surface. Results obtained led to the postulation of the formation of complexes at the adsorption sites.

It has been shown that, during the above oxidations, all the oxygen removed from the gas phase took part in the oxidation reactions.

THE STRUCTURE OF SOLIDS

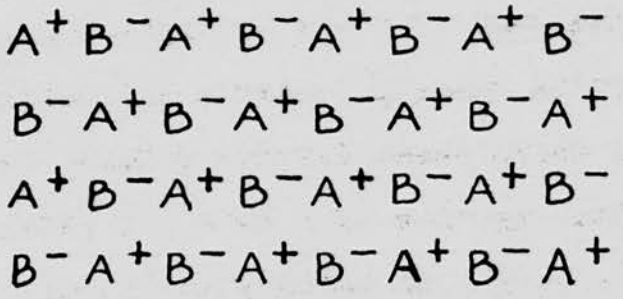
Crystalline Structure

In a perfect crystal the atoms or ions are arranged in a regular pattern throughout the crystal, the unit cell, or smallest repeating unit, being repeated in three dimensions. In ideally imperfect, or mozaic crystals, small crystal blocks which are perfect crystals in themselves are slightly disoriented. The nature of crystals of this type involving a three-dimensional network of dislocations is undoubtedly associated with structural defects such as impurity atoms, displaced atoms, surface defects, vacant lattice sites, etc. Knowledge of dislocations is restricted however to their influence on mechanical properties and crystal growth, although chemical activity of perfect and extensively dislocated structures will be signifi-:cantly different in extent, a difference paralleled of course energetically.

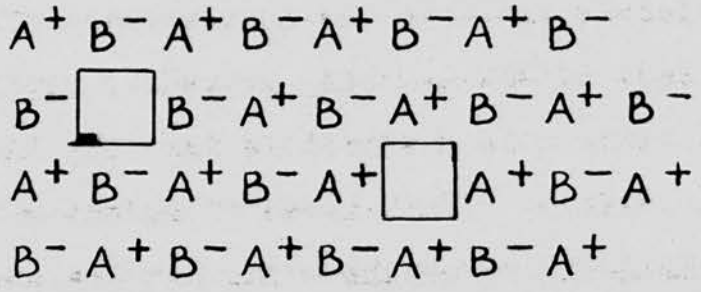
Ideal crystals have every atom and/or ion in a mean position of minimum potential energy which is equivalent to the requirements of local and long range order, involving an ordered atomic arrangement through-:out the crystal as well as among the neighbours of a particular atom.

A crystal of stoichiometric composition but having misplaced/

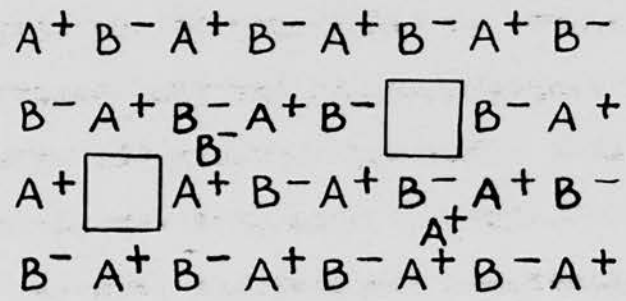
FIG. 1.



A. TWO DIMENSIONAL IDEAL LATTICE



B. LATTICE WITH SCHOTTKY DEFECTS
(A & B ION VACANCIES)



C. LATTICE WITH FRENKEL DEFECTS
(VACANCIES PLUS INTERSTITIAL IONS)

FIG. 2.

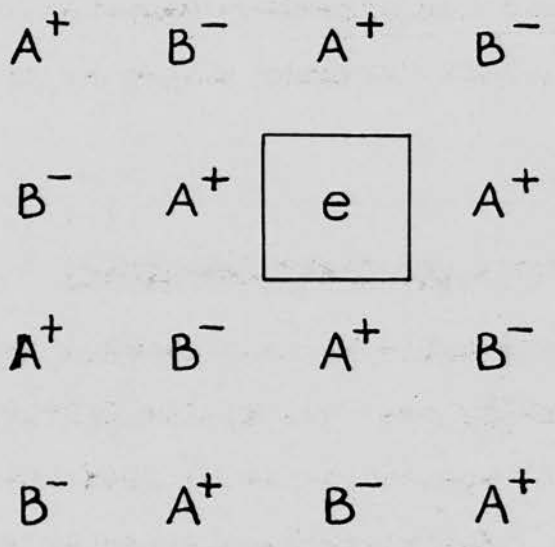
misplaced atoms or ions throughout its structure, does not have every atom or ion in a position of minimum potential energy. Such imperfect crystals are the simplest defect solids and they show two types of defect, which are the basis for the interpretation of defect solid properties, namely Schottky and Frenkel defects. Figure 1 shows these defects schematically together with an ideal lattice of a binary crystal AB. A Schottky defect is simply an unoccupied lattice site, equivalent numbers of A and B lattice sites being un-:occupied for a stoichiometric crystal.

A Frenkel defect involves the displacement of an ion to another part of the lattice, geometric require-:ments for this being more restrictive for this than for the Schottky defect. Both types of defect will cause some displacement of neighbouring lattice atoms or ions.

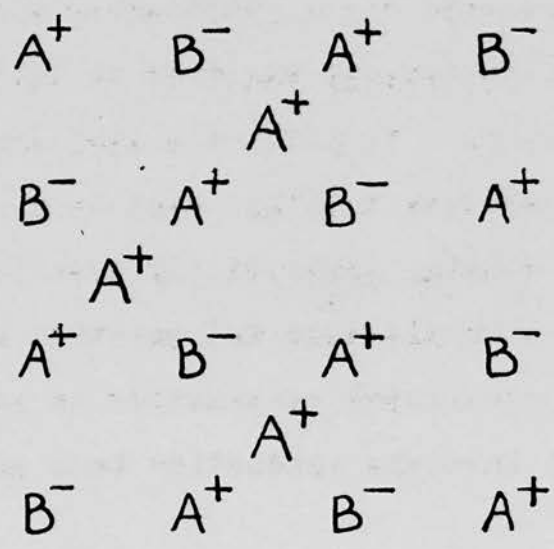
The non-stoichiometric group of crystals, in which the solids show an excess or deficiency of one component as indicated by the composition, is the most important group of defect solids. The way in which the crystal accommodates the stoichiometric unbalance depends on the nature of the excess and the possible valence states of the cations and anions.

A simple example of the type of defect present in these crystals is the F-centre (Figure 2a) in which an electron is trapped in an anionic vacancy, while the accommodation/

FIG. 2.



A. F-CENTRE



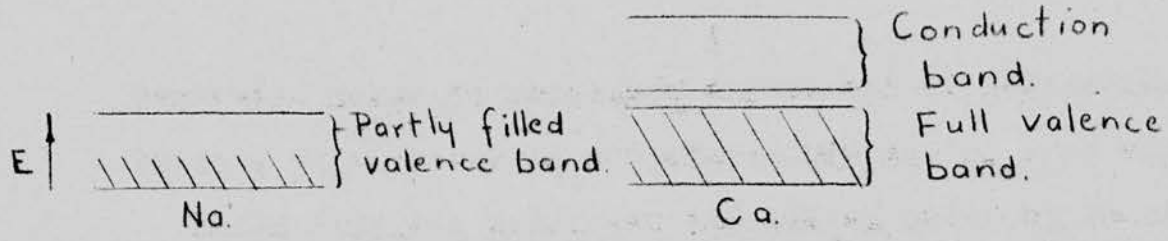
B. INTERSTITIAL CATIONS

accommodation of excess cations interstitially may occur (Figure 2b). Some substances develop an excess of the anionic component and must develop compensating vacancies in the cationic lattice. The accommodation of anions interstitially is unlikely as they are usually larger than cations. A vacant cation site will act as a centre of effective negative charge in the crystal, an anionic vacancy acting as an effective positive charge.

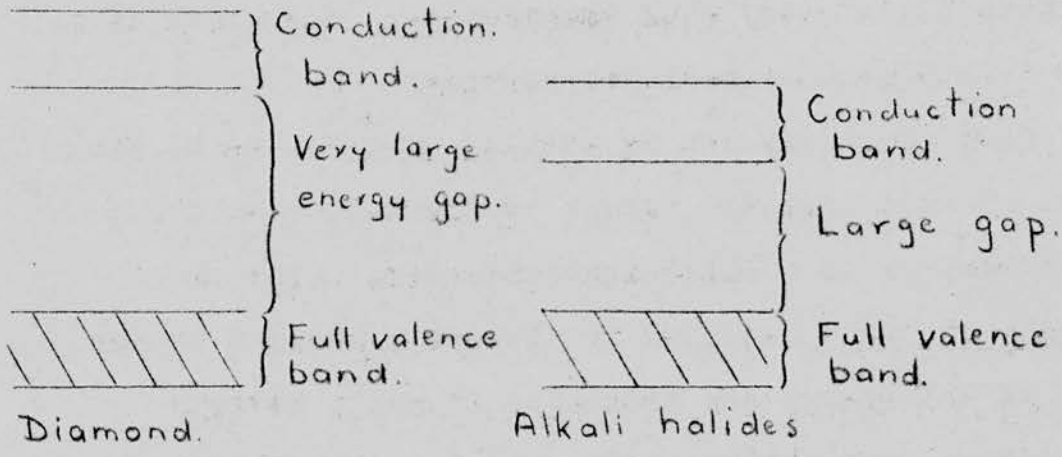
Electronic Structure and Light Absorption

The electronic orbitals in a perfect crystal are regarded as extending over the entire lattice and the electrons are not regarded as being localised at particular ions. The possible electronic energy levels for a crystal lie in a series of bands, the arrangement of which is shown, for various types of conductors in figure 3.

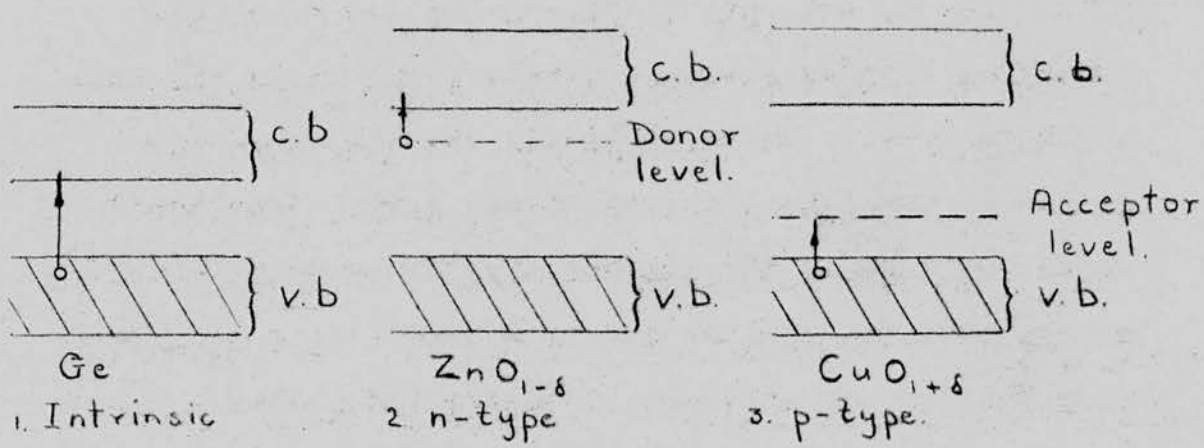
In semi-conductors the excitation of electrons occurs thermally, the energy required to excite an electron being small. In intrinsic semi-conductors an electron is excited from a filled band to an empty band leaving a positive hole, conductivity resulting from the migration of both electron and positive hole. In an n -type semi-conductor an electron is excited from an impurity level into the conduction band and conductivity/



(a) Metallic Conductors.



(b) Insulators.



(c) Semi-conductors.

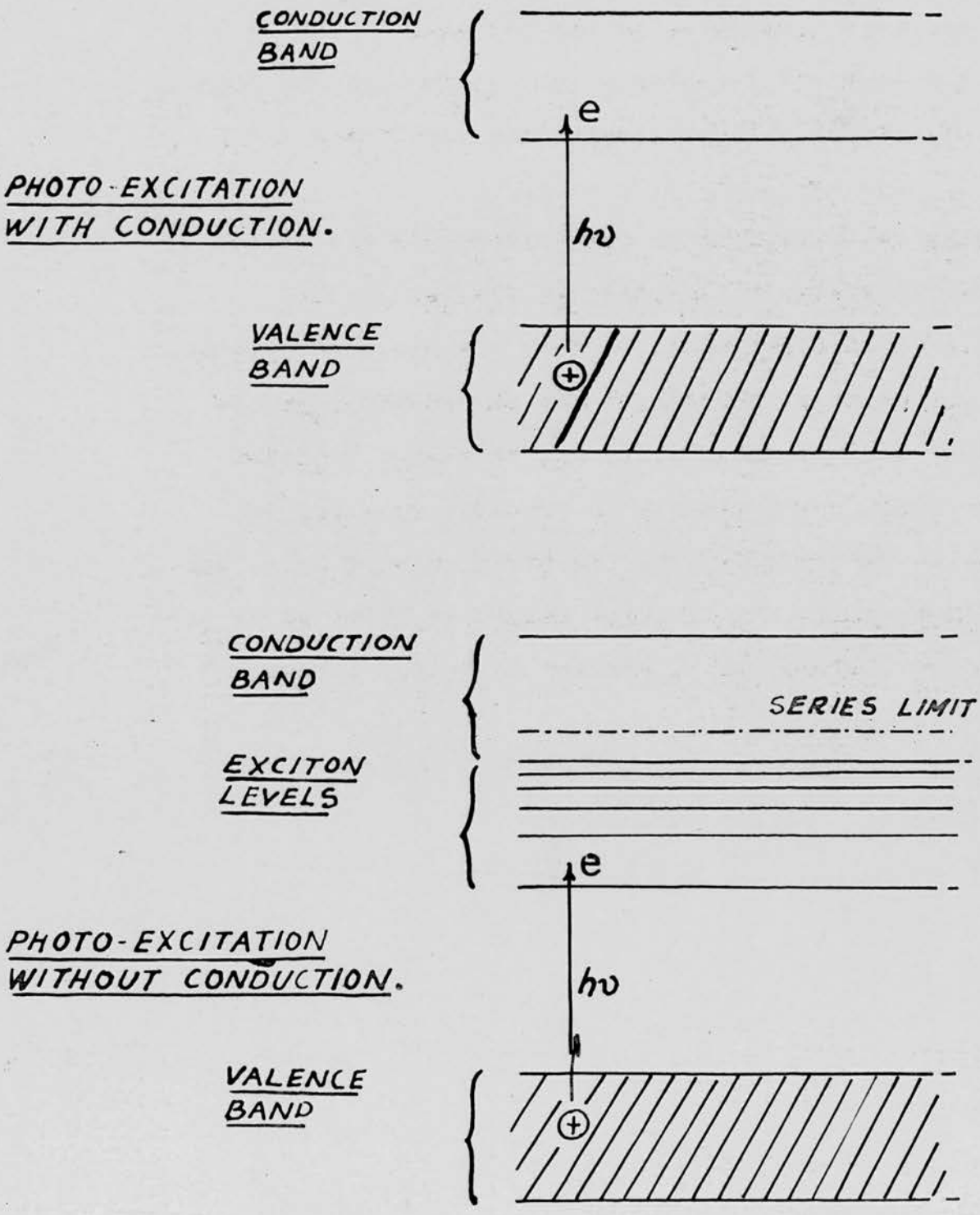
Fig. 3.

conductivity is due to the migration of these electrons while in a p-type semi-conductor an electron is excited into an impurity level, the resulting positive holes being responsible for conduction. When the energy gap is so large that electrons can only be excited sufficiently at very high temperatures, the solid is a good insulator at normal temperatures.

When electrons can be excited into the conduction band, or into acceptor levels by the action of light the substance is a photo-semiconductor. The wave-:length of light required is obviously related to the size of the energy gap occurring normally between valence and conduction bands, but in some solids, absorption of light of longer wavelength than that which gives rise to such photoconductivity can occur in-:dicating excited electron levels lying below the con-:duction band. In these levels the electrons are localised near the positive holes, giving "excitons" which can migrate through the crystal by transfer of energy from the excited ion or molecule to a neighbour-:ing like ion or molecule in the ground state. There may be a series of exciton levels leading to a series limit within the conduction band, leading to dissociation of the electron and positive hole (Figure 4).

Photoconductivity, then, results from the migration of/

FIG. 4.


CONDUCTION BAND
e
PHOTO-EXCITATION WITH CONDUCTION.
hν
VALENCE BAND
CONDUCTION BAND
SERIES LIMIT
EXCITON LEVELS
e
PHOTO-EXCITATION WITHOUT CONDUCTION.
hν
VALENCE BAND

of excited electrons or positive holes or both, while the production of excitons occurs without giving rise to conduction. The excited electrons regain their ground state either by a radiationless transition, emission of light of longer wavelength than that absorbed, in fluorescence or phosphorescence, or by causing a chemical reaction at the surface of the solid. Fluorescence and phosphorescence are associated with impurity type semiconductors only.

Chemical reactions on the surface are caused by transfer of energy to an adsorbed species or the transfer of an electron to or from the adsorbed species, while the terms photocatalyst and photosensitiser are correctly employed when referring to energy transfer of this type, their meaning is commonly extended to include charge transfer, in reactions of zinc oxide and titanium dioxide such as those mentioned above as it is by no means certain which process is taking place.

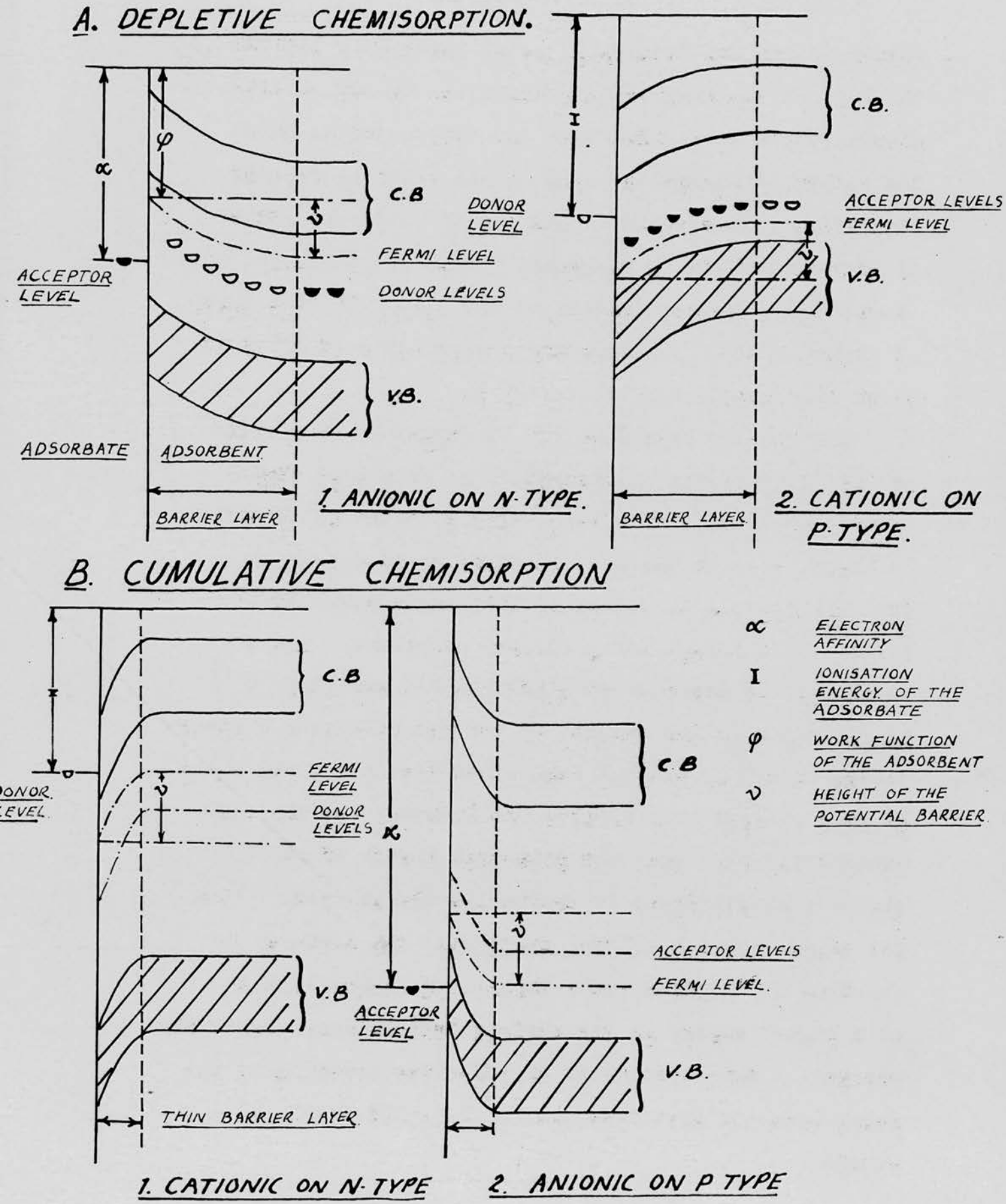
CHEMISORPTION AND CATALYSIS IN OXIDE SEMICONDUCTORS

In any catalytic reaction one at least of the reactants must be adsorbed on the catalyst surface and the mechanism of adsorption on the surfaces under in-:vestigation must be understood before any theory of catalysis can be constructed.

The idea that specific chemisorption sites with localisation of electrons existed on the surface of a catalyst and that electron transfer to and from these sites took place on chemisorption, has been widely developed, and theories, to explain the fall in differential heats of adsorption with surface coverage, have been put forward. The factors considered include intrinsic heterogeneity, induced heterogeneity and re-:pulsive interaction which are important in low, medium and high surface coverages respectively. Frenkel steps, dislocations and crystal edges will pro-:vide sites of high adsorption energy which will form part of the intrinsic heterogeneity of the solid. The boundary layer theory explains the fall in heats of adsorption by postulating the formation of a space charge on chemisorption, giving induced heterogeneity, and repulsion of charged chemisorbed molecules will take place at high surface coverage.

The boundary layer theory is particularly useful in attempts to correlate semiconductivity with chemisorption/

FIG. 5.


A. DEPLETIVE CHEMISORPTION.
α
φ
ν
C.B
DONOR LEVEL
FERMI LEVEL
DONOR LEVELS
ACCEPTOR LEVEL
V.B.
ADSORBATE
ADSORBENT
BARRIER LAYER
1. ANIONIC ON N-TYPE.
I
C.B.
ACCEPTOR LEVELS
FERMI LEVEL
V.B.
BARRIER LAYER
2. CATIONIC ON P-TYPE.
B. CUMULATIVE CHEMISORPTION
C.B
FERMI LEVEL
DONOR LEVELS
V.B
THIN BARRIER LAYER
1. CATIONIC ON N-TYPE
C.B
ACCEPTOR LEVELS
FERMI LEVEL.
V.B.
ACCEPTOR LEVEL
2. ANIONIC ON P TYPE
α ELECTRON AFFINITY
I IONISATION ENERGY OF THE ADSORBATE
φ WORK FUNCTION OF THE ADSORBENT
ν HEIGHT OF THE POTENTIAL BARRIER

chemisorption and catalysis, as it takes into account the type of semiconductivity exhibited by the adsorbent. Chemisorption is divided into two types, one in which the number of charge carriers in the solid is reduced, -depletive chemisorption - and one in which the number of charge carriers is increased - cumulative chemi-:sorption. The application of the theory to both types of chemisorption on n-type and p-type semiconductors is shown diagrammatically in figure 5.

The case of chemisorption of oxygen on zinc oxide is one of depletive chemisorption on an n-type semi-:conductor. Initially Fermi levels in the solid will be higher than in the gas and transfer of electrons from donor levels in the solid will occur with the formation of a negatively charged adsorbate. As a result of the transfer of electrons and emptying of donor levels in the surface of the semiconductor a space charge is set up with an associated electric field which gives a voltage drop between the interior and the sur-:face traps such that the potential energy of an electron increases as it approaches the surface. Thus the energy of each allowed state near the surface in-:cluding the surface states themselves become located at a higher energy as the surface becomes more negatively charged. This results in an effective lowering of the Fermi level of electrons within the solid until it equals/

equals the potential energy of electrons in the adsorbate. During depletive chemisorption equilibrium will be reached before a monolayer of adsorbate is complete as the number of adsorbed molecules at equili-:brium is controlled by the number of donor or acceptor centres in the solid.

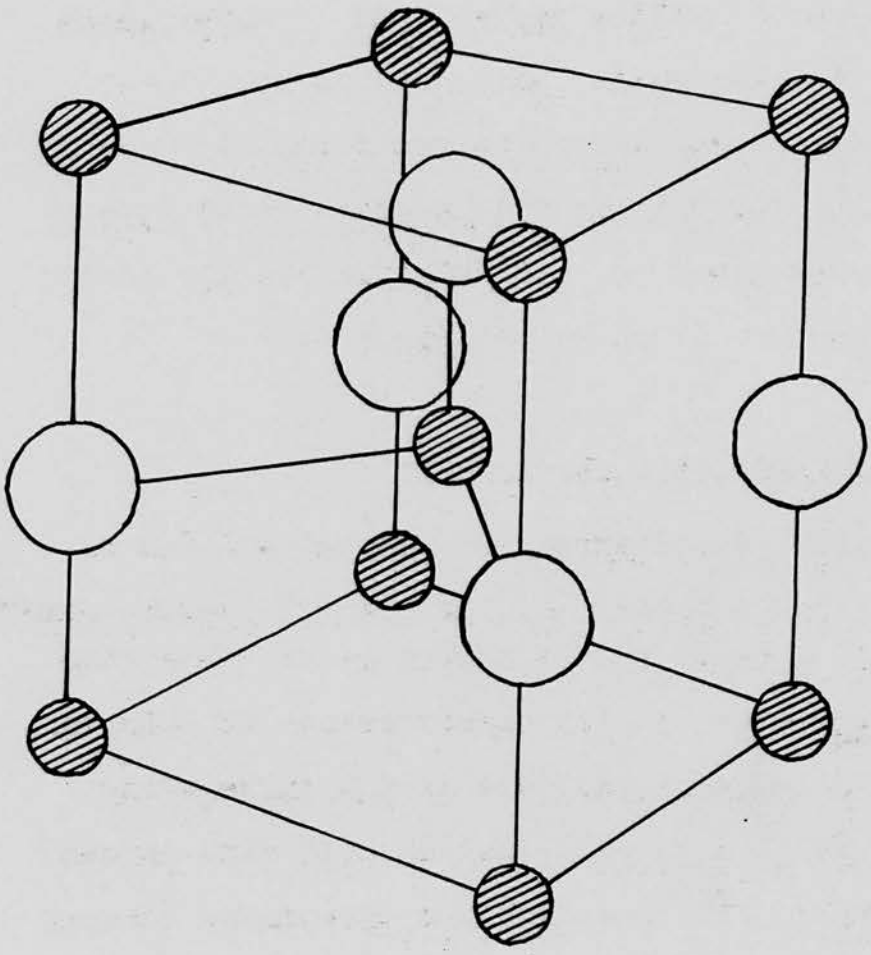
During cumulative chemisorptien the number of molecules which can be adsorbed is limited by the number of donor or acceptor centres which can be established in the solid. As the density of the energy levels in the empty conduction band and the full valence band is high this number is generally large, and the chemisorption is limited by the geometry of the surface, a monolayer being formed.

Theoretical work on the kinetics of chemisorption has been concerned with explaining the equation of the Roginsky Zeldovich type i.e.

$\frac{dq}{dt} = ae^{-q/t}$ where q is the amount chemisorbed in time t.

Generally the data are consistent with activated chemisorption occurring with an increasing energy of activation. The Boundary Layer theory and surface heterogeneity have been proposed to explain the increase in activation energy with surface coverage, while in some cases surface migration of the adsorbed species is considered to be rate determining.

FIG. 6.



ZINC OXIDE

STRUCTURE OF ZINC OXIDE

Crystal Structure

Ionic crystals of the AX type are divided into six types, each with a typical unit cell, named after a particular compound forming crystals of that type e.g. NaCl-type lattice. The ionic nature of crystals form-:ing each type of lattice varies, the NaCl-type being formed by ionic compounds, while ZnS is relatively covalent and covalent compounds can form this type of crystal. The ZnO-type lattice appears to be inter-:mediate between the NaCl- and ZnS-type and the unit cell for this type is shown in figure 6.

Electronic Properties of Zinc Oxide

Zinc oxide is a diamagnetic crystal and its Zn^{++} ions have filled d-bands. It is now well established[23] that unfilled d-bands in the structure of transition metals are essential to the chemisorption of hydrogen. A zinc metal film will only act as a hydrogenating catalyst if it is purposely contaminated with oxygen after preparation[24] and inactive zinc oxide becomes active after treatment in vacuo or hydrogen. This suggests that the active form is an intermediate between ZnO and Zn, possibly non-stoicheometric ZnO.

The existence of non-stoichiometric ZnO has been recognised for some time and an equilibrium between ZnO/

ZnO and O_2 in the gas phase at high temperature has been proposed whereby excess zinc can be accommodated interstitially in the lattice, these atoms being subject to thermal ionisation and so providing donor centres. Conductivity measurements[25,26] show that equilibrium sets in rapidly at temperatures as low as 500° C. and the defect equilibrium can only be realised in a sur-:face layer; at temperatures below this, the equilibrium cannot be reached in finite time. When non-stoichio-:metric ZnO is heated in oxygen a slow decrease in conductivity is noted as oxygen is taken up indicating the trapping of conduction band electrons. Conversely heating in hydrogen increases the conductivity of ZnO.

An alternative view of the activation of ZnO by removal of oxygen is that a chemisorption of Zn on ZnO may occur, a system intermediate between ZnO and Zn again being established.

The application of the properties of the bulk material to the surface layer must be regarded with caution. Thus with ZnO, the surface may show very low conduction due to the adsorption of oxygen, or very high conduction due to removal of oxygen in vacuo, irrespec-:tive of the composition of the bulk material. Morri-:son[27] from his own results and the work of Bevan and Anderson[26] has proposed a model for chemisorption to explain the dark conduction. Physically adsorbed oxygen/

oxygen forms acceptor sites for conduction electrons and traps them forming O^-, bound to the lattice by the electric field set up by Zn^+ ions, while Melnick has suggested that photoconductivity in zinc oxide is due to the transformation of chemisorbed oxygen surface ions by light to the neutral physically adsorbed species.

The overall view would appear to be that when ZnO electrons are thermally excited they can be trapped by oxygen physically adsorbed on the zinc oxide and photo-produced electrons can be similarly trapped.

It would appear that conduction electrons (either thermally or optically excited) can be trapped by physically adsorbed oxygen and thus removed from the conduction band. Heating and illuminating zinc oxide results in increased conductivity, more conduction electrons becoming available with time until an equili-:brium is reached. This would appear consistent with either the conversion of chemisorbed oxygen to the physically adsorbed type or the conversion of lattice oxygen to physically adsorbed oxygen with the production of new donor sites.

Photoconductivity

When a semiconductor is illuminated, electrons may be excited into the conduction band, and/or holes into the valence band, producing photoconductivity. This condition/

condition is not permanent, and when illumination ceases, the excited electrons or holes decay or recombine. Excitation of electrons from the valence band with simultaneous production of positive holes takes place in many semiconductors and recombination of electron and hole at surface traps is considered likely. A change in number or energy of these surface traps, or change in the height of the surface barrier may affect the rate of recombination.

Photoconductivity in zinc oxide, however, appears to be influenced by the surface, in a different way, absorption of light exciting electrons trapped at surface levels into the conduction band. Melnick considers the nature of these trapping centres to be chemisorbed oxygen atoms which are liberated as physically adsorbed oxygen on illumination. Photoconductivity decays, on the other hand, with the adsorption of oxygen.

Photoconductive response appears to be divided into fast and slow responses. The fast responses, rise or decay of photocurrent having time constants of a second or less have been interpreted by Malwo, et al[28,29,30], Weiss[31] and Heiland[32,33] as bulk processes, associated with the double ionisation of interstitial zinc and have proposed that a photon excites an electron from the valence band and the hole produced/

produced immediately combines with the electron from an interstitial Zn^{+} ion, producing Zn^{++} ions.

Evidence indicates that the slow response is associated with the surface. Heiland ([32,33]) has found that illuminating ZnO in vacua produced a photocurrent which remained stable after illumination ceased until oxygen was admitted to the surface.

Melnick[13,34] has made the most extensive study of the slow response and observes that the rise and decay curves obey the Elovich equation $q = ae^{-bq}$ if conductance (K) is directly related to the quantity of gas adsorbed (q) giving the following equation

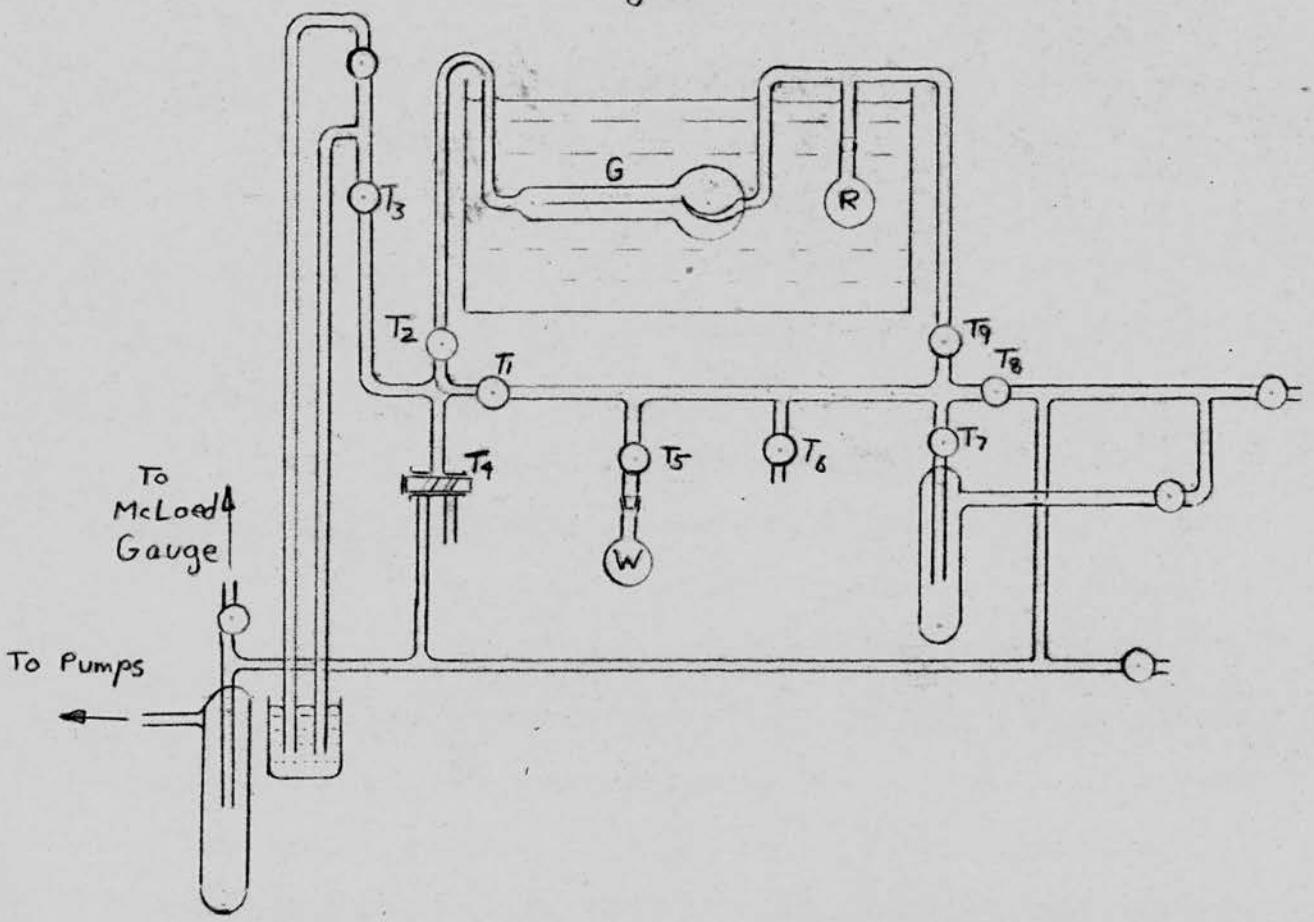
$K = ae^{-bk}$ where a and b are constants.

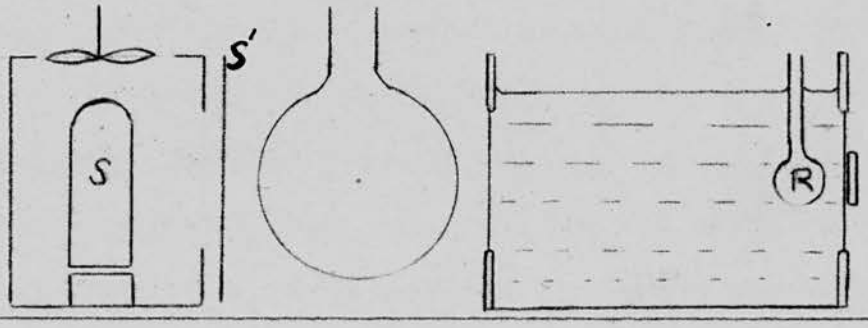
He observed that photoconductivity was retarded and decay accelerated by increased oxygen pressure. Melnick also noticed that if a sample which was decaying at room temperature was rapidly cooled to 130° K. the decay ceased and continued, from the same point on restoration of the sample to room temperature.

Melnick has suggested that the fast response is also due to surface effects having the same reactions and model as the slow response, which are briefly as follows. The absorption of light leads to the creation of an electron positive hole pair. The positive holes diffuse towards the surface and combine with electrons from O^{-} levels, the O^{-} electron returning to the crystal and the oxygen atom formed being desorbed.

APPARATUS, CHEMICALS and EXPERIMENTAL TECHNIQUES

Figure 7a





A P P A R A T U S

APPARATUS FOR SORPTION MEASUREMENTS

The principle functions of the apparatus, shown in figure (7a), were the evacuation of a film of zinc oxide, prepared on an inside face of the vessel R, and the measurement of small pressure changes, in a constant volume, occurring when the film was illuminated, by source S, in contact with various gases.

Evacuation was by a mercury diffusion pump, backed by a Hyvac pump, giving a pressure of 10^{-5}mm(Hg) as measured by a McLoed gauge incorporated in the system.

A Bourdon gauge G. was used to measure changes in pressure occurring in the reaction space R, the platinum tip of the gauge pointer being observed through a telescope with an eyepiece scale. The Bourdon gauge was made of soda glass as was most of the apparatus; ground glass taps and joints were used where necessary and were lubricated with Apieson L grease.

As the Bourdon gauge is very sensitive to temperature fluctuations, both the gauge and flask R were immersed in a glass sided thermostat tank. The water was heated by an electric heater, 250 watts, in series with a 200 ohm resistor, controlled by a volume and mercury regulator, through a valve relay. Water circulation was by an external centrifugal pump. This arrangement/

arrangement gave a temperature stability of $\pm$ 0.01°C. at a fixed point in the tank.

The line connecting the reaction space with the gauge jacket had two side arms with taps and ground-glass cones to enable zinc oxide films to be evacuated and condensable gases to be withdrawn from and admitted to the system. A cold trap connected to the reaction space lead allowed condensable constituents in gases from the reaction space to be collected. Provision was made to admit gases, from a set of storage bulbs, to the system.

Steady gas pressures were measured by the mano-:meter or the Bourdon gauge.

Illumination was by white light from a Mazda 250W mercury lamp, focused by a flask containing a solution of copper sulphate (≡ 1 cm. of a solution of 100 g. $CuSO_4 . 5 H_2O$ per litre) which also acted as a heat filter. The lower limit of illumination λ = 3200 Å was set by the glass in the system. To vary the light intensity or isolate light of λ = 3650 Å, optical filters were placed inside the thermostat tank, neutral filters being used in the former case and a 2 mm. Wood's glass filter in the latter. A photo-cell and sensitive low resistance galvanometer were used to check the intensity of the light transmitted by the zinc oxide film. Over the range of intensities used, the/

Figure 7c

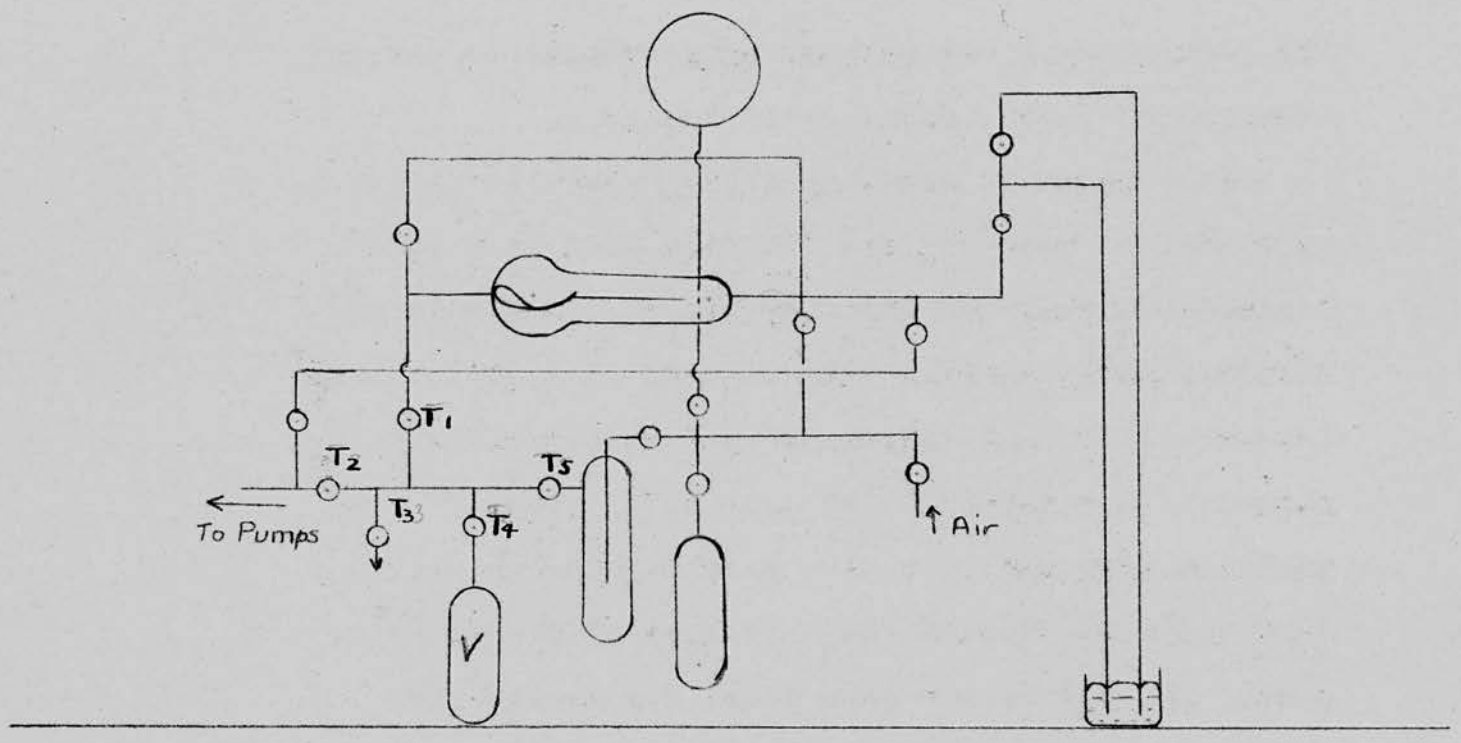
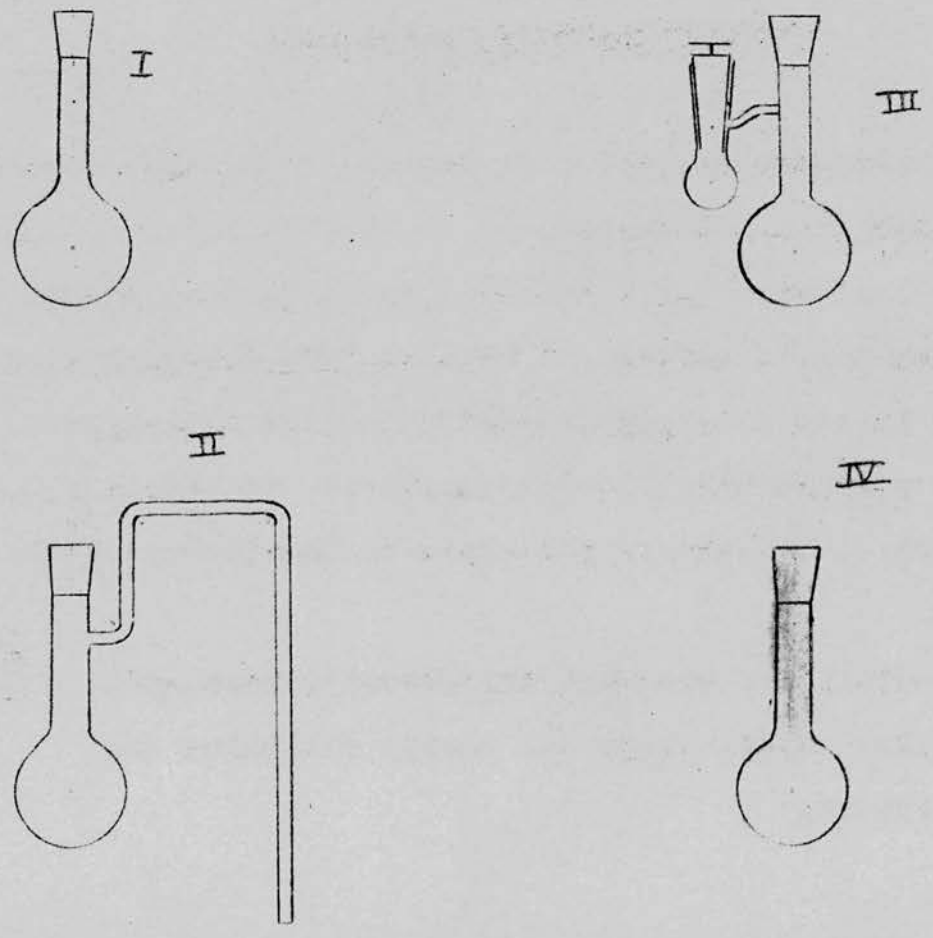


Figure 7b



the photocurrent was assumed proportional to the in-:tensity of light impinging on the cell.

Four types of reaction flask, shown in figure (7b), were used. Types II and III were used to remove condensable material from the reaction space during sorption measurements, the side arm of type II being immersed in liquid oxygen and phosphoric oxide being placed in the side-arm of type III. Type IV was used whenever possible as a more regular zinc oxide film could be prepared in this type of flask. The ground glass joint in this flask was sealed with Apiezon L grease.

APPARATUS FOR GAS PURIFICATION AND VAPOUR PRESSURE MEASUREMENT

The apparatus, shown in figure (7c), consisted of two vessels separated by a cold trap in which vapours could be condensed and purified by distillation from one vessel into another. Vapours were expanded from vessel V into a soda-glass Bourdon gauge for vapour pressure measurement; the temperature of vessel V was measured by a thermocouple taped to the bottom of the vessel.

As only low pressure measurements were made (< 3mm) the jacket of the gauge was always evacuated and thermostating/

thermostating was not necessary.

A side-arm with a ground-glass cone was provided to allow vapours to be admitted to and withdrawn from the system.

The apparatus was connected to the main vacuum line of the apparatus for sorption measurement.

SOURCE, PREPARATION AND PURIFICATION OF CHEMICALS

Zinc Oxide Hyperfine

Zinc oxide hyperfine was prepared by the method of Conn, Humphrey, Magee and Wallace (22) as follows.

14.7 g. zinc oxide A.R. (B.D.H.) were stirred into a solution of 13.5 g. ammonium carbonate in 67 ml 8N ammonia, a small amount of zinc oxide remaining undissolved at room temperature. The solution was filtered and carbon dioxide was bubbled through the filtrate, with stirring, until precipitation of zinc carbonate ammoniate ($ZnCO_3 . NH_3$) ceased (about 5 hours). The crystals were filtered off and heated at 250°C, with periodic agitation until no further evolution of ammonia could be detected with litmus. A brick-red finely divided powder was obtained.

The further removal of ammonia and carbon dioxide was then undertaken by the following methods yielding samples with different ammonia contents.

Sample I

Heated at	250° ± 5°C. in air for 1 day
Ammonia Content	168 μ moles/g.

Sample II (a)

Heated at	250°C. in air for 2 days
Ammonia Content	218 μ moles/g.

Sample/

Sample II (b)

Heated at 250°C. at 10mm. (Hg) for 2 days

Ammonia Content 41.9 μ moles/g.

Sample III

Heated at 250°C. with pumping by Hyvac oil pump for 5 days, final pressure with mercury diffusion pump 10^{-5}mm. (Hg) for 1 day.

Ammonia Content = 26.4 μ moles/g.
= 26.7 μ moles/g.
} Average 26.6 μ moles/g. ZnO

The ammonia present in these samples was determined using Nessler's reagent (page 40).

Oxygen

B.O.C. cylinder. Condensable impurities were removed before storage by passing the gas through a cold trap at liquid oxygen temperature. The gas was stored in a glass bulb attached to the apparatus.

Nitric Oxide

Nitric oxide was prepared as follows.

A solution of 17g. sodium nitrite and 40g. potassium iodide in 100 ml. water was placed in a conical flask fitted with a dropping funnel and outlet tube. The apparatus was flushed out with carbon dioxide and a solution of hydrochloric acid (50ml.conc. hydrochloric acid/

acid and 50ml. water) was added dropwise, nitric oxide being produced according to the equation.

$$2\ NO_2^- + 4\ H^+ + 2I^- \rightarrow 2\ NO + I_2 + H_2O$$

The nitric oxide was passed through concentrated sulphuric acid and 50% potassium hydroxide solution to remove iodine before being absorbed in a cold solution of ferrous sulphate containing 100g. ferrous sulphate in 2L. of solution.

The nitric oxide was regenerated, by warming the ferrous sulphate solution and was passed over phosphoric oxide to remove water vapour before being condensed in a cold trap at liquid oxygen temperature. Non-con-:densable impurities were removed by pumping with a Hyvac pump and condensable impurities, mainly nitrous oxide were removed by repeated fractionation at low temperatures. The nitric oxide obtained was at least 99.9% pure, no material condensable at liquid oxygen temperature being detectable, and adequate evacuation having been given to the nitric oxide in a liquid oxygen cooled trap, to remove all non-condensable gases. The nitric oxide was stored in a glass storage bulb attached to the apparatus.

Ammonia

Ammonia was prepared by the dry distillation of calcium oxide and ammonium chloride

$$CaO + 2\ NH_4Cl \rightarrow CaCl_2 + 2\ NH_3 + H_2O$$

The/

The gas was passed through a soda lime tower to remove traces of carbon dioxide and some water and distilled from a cold trap at .-80°C, the middle fraction of the distillate being collected. The gas was now distilled over potassium hydroxide into a glass storage bulb. The purity was at least 99.5%, no im-:purities being detectable on distilling the ammonia from a cold trap at -120°C.

Nitrous Oxide

Elliot and Co. (Edin.) cylinder nitrous oxide was distilled from a cold trap at approximately -150°C. into the apparatus for vapour pressure measurements, for use as a standard.

Carbon Dioxide

Solid carbon dioxide (I.C.I.) was purified by re-:peated distillation at < 1 cm. pressure into a cold trap at liquid oxygen temperature for use as a standard in the identification of substances by vapour pressure measurements.

Acetone

Hopkins and Williams, A.R. grade, containing,not more than 1% water, and 95% acetone.

Griess/

Griess-Ilosvay Reagent (35)

A solution of 0.1g. α -naphthylamine in 10 ml. glacial acetic acid and 40 ml. water was added to a solution of 0.5g. sulphanilic acid in 10 ml. glacial acetic acid and 40 ml. water and the mixture made up to 250 ml. with water. The reagent was stored in a stoppered flask in the dark.

EXPERIMENTAL TECHNIQUES

Calibration of the Bourdon gauge

Before changes in pressure occurring in the reaction space could be converted into mm. (Hg) the sensitivity of the Bourdon gauge in mm/division had to be found.

The system was evacuated and the gauge jacket, connected to the manometer, was isolated from the re-:action space until a Bourdon gauge scale reading of about 20 divisions was obtained when the system had reached equilibrium. The manometer and gauge scale readings were noted and air was admitted to the gauge jacket until the gauge scale reading was about 80 divisions. The system was allowed to regain equili-:brium, when the gauge scale reading was noted. Air was now admitted to the reaction space until the gauge scale reading was again about 20 divisions and the reading noted with the system in equilibrium. Air was admitted to the jacket as before and these operations were repeated until a pressure of about 200 mm. was recorded on the manometer with the gauge pointer at the bottom of its travel (about 80 divisions).

The manometer reading was noted and the total change in pressure which had taken place in the gauge jacket was calculated. The total downward travel of the gauge pointer, that is, the movement taking place during/

during admission of air to the gauge jacket, was calculated and the sensitivity of the gauge calculated as

$$\frac{\text{Total change in pressure in gauge jacket}}{\text{Total downward movement of gauge pointer}} \text{ mm(Hg)/division}$$

The average value for several calibrations was taken as the gauge sensitivity.

Example

Total Pressure Change (Manometer) mm(Hg)	Total Gauge Travel divisions	Gauge Sensitivity mm/division
17.1	308.6	0.0554
19.0	349.0	0.0544
19.6	352.7	0.0555

Average Gauge Sensitivity = 0.0551 mm/division

The sensitivity of this type of gauge is known to be independent of total pressure in the range 0-200 mm (Hg).

Determination of Reaction Space Volume

It was necessary to find the volume of the reaction space before pressure changes occurring in it could be converted into molar quantities.

In order to measure this volume, the volume of flask/

flask W and the lead from it up to and including the bore of tap T_5, was measured by weighing them, first empty and then full of water at known temperature. After reconnecting flask W to the apparatus, and following thorough evacuation, air was admitted to the apparatus until the pressure was about 300 mm., and the manometer reading recorded. Taps T_4 and T_9 were closed and flask W and the leads from it to the re-:action space were evacuated. Tap T_5 was then closed and the air from the reaction space was expanded into the leads between the reaction space and tap T_5, while air was pumped out of the gauge jacket to keep the gauge pointer at its equilibrium position. When the expansion was complete the pressure was read from the manometer. Tap T_5 was now opened and air from the reaction space and the leads was expanded into flask W, the gauge pointer being kept in its equilibrium position as before. The new pressure was read from the mano-:meter.

The volume of the reaction space was calculated from the pressure measurements and the volume of flask W.

Example

Volume of Reaction Space = V_1

Volume of Leads = V_2

Volume of Flask W = V_3 = 47.80 ml.

Gas/

Gas Pressure in V_1 $= P_1 = 300.8$ mm.

Gas Pressure in $V_1 + V_2$ $= P_2 = 200.6$ mm.

Gas Pressure in $V_1 + V_2 + V_3$ $= P_3 = 131.4$ mm.

The volume in the reaction space is given by

$$V_1 = \frac{P_2 P_3 V_3}{P_1 (P_2 - P_3)}$$

By substitution

$$V_1 = \frac{200.6 \times 131.4 \times 47.8}{300.8 \times 69.2}$$

$$= 60.58 \text{ ml.}$$

On Repetition $V_1 = 60.41$ ml.

Volume of Reaction Space = 60.5 ml.

Preparation of Powder Films

Zinc oxide films were prepared using either acetone or water as the binding liquid. In the case of acetone a small amount of oxide (0.01 to 0.1g.) was accurately weighed into a reaction flask and about 1 ml. of acetone added. A suspension was formed and this was spread uniformly into a film of about 3 cm. diameter on the reverse face of the flask. Air was blown over the film and when dry it was attached to the high vacuum apparatus by a ground glass joint and pumped to 10^{-4} to 10^{-5} mm(Hg) at room temperature for at least 5 days. When water was used to prepare films in flasks of type I, II or III a paste film was prepared as before. The/

The flask was now attached to a water pump and warmed until the water had evaporated and the film appeared dry. The flask was now attached to the high vacuum apparatus and pumped as in the case of acetone bound films. Films prepared by these methods were not even and a more regular film was prepared in flasks of type IV by the following method. Zinc oxide was weighed out into the removeable end of the flask and enough water added to give mobility to the powder. A sus-:pension was formed and allowed to settle, the flask end being placed in a desiccator. After standing in the desiccator for 12 hours the film was dry and the flask was reassembled and attached to the high vacuum apparatus for pumping as in previous cases. Although this film was saturated with water for several hours this did not appear to affect its sorptive properties as compared with those of a film prepared by rapid evaporation of water in a similar flask. Films pre-:pared in type IV flasks showed an increased sorptive capacity over those prepared in flasks of types I, II and III. This is attributed to the more even distri-:bution of powder particles in the film.

On pumping all films gave off water and carbon dioxide in appreciable quantities. The films were pumped for about 8 hours a day and stood in contact with a cold trap at liquid oxygen temperature overnight. After/

After 5 days of this treatment the evolution of water and carbon dioxide was very slow. The removal of water and carbon dioxide are described fully on page (61).

Oxygen Uptake Isotherm

The mercury lamp was allowed to warm up for some time before starting illumination, and the thermostat bath was allowed to reach equilibrium. Oxygen was admitted to the reaction space while dry air was admitted to the gauge jacket to maintain the gauge pointer in its equilibrium position. The reading on the manometer gave the gas pressure. Taps T_1 and T_9 were closed and gauge readings were taken for some minutes. These readings served as a check for tempera-:ture fluctuations since no observable dark uptake of oxygen takes place.

The film was now illuminated by removing shutter S' and changes in pressure (ΔP) were recorded by reading the gauge to the nearest 0.1 div. at intervals of several minutes. When the gauge pointer neared the limit of the scale it was rapidly raised to a position above its equilibrium position, by pumping air out of the gauge jacket.

The values of ΔP were plotted against time (t) of illumination and a smooth curve was drawn through the points.

In/

In some cases it was necessary to interrupt the illumination and it was shown in some preliminary experiments (p. 54) that interruption of illumination causes only a very slight elevation of the rate of uptake, which becomes appreciable only if the film is allowed to stand in vacuo. A smooth ΔP against t curve could therefore be drawn through the values obtained, including periods when the film was not illuminated.

An oxygen pressure of 50 mm (Hg) was normally used; as the total pressure decrease during an illumination was less than 3 mm (Hg) the oxygen pressure remained effectively constant. It was later shown (p. 92) that the rate of uptake is independent of the oxygen pressure in this pressure region.

Rate Curves

The ΔP against t curve obtained as above was divided into intervals of time during which the same pressure change occurred. The rate value R was obtained by dividing the pressure change occurring in each section by the time during which this change occurred. The rate values were plotted against the total change in pressure $\Sigma \Delta P$ which had occurred up to the middle of the section for which a value of R was obtained, giving a "rate curve" of R against $\Sigma \Delta P$

Various/

Various functions of R and $\Sigma\Delta P$ were used to give linear rate plots which could be extrapolated to give the total pressure change at infinity. In particular the rate plot of R against $\log \Delta P$ was widely used.

Relative Rate Method

The effect of varying such parameters as pressure, temperature and light intensities, on the rate of oxygen uptake was investigated by means of the relative rate method, as follows. An oxygen uptake isotherm was obtained for a system in which a particular parameter X has the initial value X_1. When sufficient information had been obtained to plot an R against $\log (\Sigma\Delta P)$ graph the value of X was changed from X_1 to X_2 and an isotherm obtained which gave a new R against $\log (\Sigma\Delta P)$ line. Other values of X were now used and the process repeated for each value. Finally the value of X was returned to X_1 whenever possible and more values of R and $\log(\Sigma\Delta P)$ were obtained.

A linear R against $\log(\Sigma\Delta P)$ plot for each value of X was obtained and these lines were then extrapolated to obtain a value of $\log (\Sigma\Delta P)$ at R = 0, the same value being obtained for each line. A line was now drawn to intersect all the lines at an arbitary value of $\log(\Sigma\Delta P)$. The rate value at each intersection was divided by that at the intersection of the $X = X_1$ line. The/

The values obtained were the relative rates (R.R.) for values of X, the relative rate at $X = X_1$ being unity.

Vapour Pressure Measurements

During illumination of a zinc oxide film in oxygen, nitric oxide or oxygen and ammonia, or during the sorption of ammonia in the dark by zinc oxide, con-:densable substances were liberated into the gas phase.

The condensable substances were collected free from oxygen and nitric oxide by pumping the gas phase through a cold trap at liquid oxygen temperature. The contents of the cold trap were transferred to the vapour pressure apparatus (p.24), and degassed by repeatedly warming them to room temperature, rapidly freezing them out and pumping away noncondensable material. Mixtures were now separated by repeated fractionation at very low pressures (about 0.1 mm). The pure substances obtained were collected in vessel V (fig. 7c) which was connected to the Bourdon gauge through tap T_1, taps T_2, T_3 and T_5 being closed. The Dewar vessel of liquid O_2 surrounded vessel V at this stage was removed, the liquid oxygen poured out and the empty vessel replaced as quickly as possible. As vessel V slowly warmed up, the vapour pressure of its contents was indicated on the Bourdon gauge and its temperature measured by a thermocouple taped onto the bottom of vessel V.

The/

The vapour pressure of water was measured with vessel V surrounded by a bath of petroleum ether (B.P. 20° - 40°C.) which was cooled to suitable tempera-:tures which were measured with a calibrated thermometer.

The vapour pressures measured were compared with those of known substances measured in the same way or with values obtained from International Critical Tables, in order to identify the substances obtained.

The volume of vessel V and its leads to the Bourdon gauge was measured and the amounts of materials obtained during sorption measurements were calculated from their pressure in this volume at room temperature.

The measurement of amounts of water by this method was liable to error due to sorption by the vessel surfaces. At the pressures and temperature used in these measurements, however, this error will be small enough to be ignored.

Estimation of Ammonia in Zinc Oxide

Zinc oxide hyperfine, which was prepared from zinc carbonate ammoniate (p. 26), contained ammonia as an impurity. As it is shown later that the presence of ammonia on the surface of zinc oxide affects its uptake of oxygen, it was important to know the amount of ammonia in the samples prepared.

Approximately 0.1 g. of zinc oxide was weighed out accurately/

accurately and dissolved in dilute sulphuric acid. Sodium hydroxide solution was added until a slightly alkaline solution was obtained. The solution was made up to 50 ml. with water.

A 20 ml. sample was taken and 2 ml. Nessler's reagent was added. The extinction coefficient of the solution at λ = 450 mμ was measured against a blank solution prepared as above, but without zinc oxide, using a Unicam S.P. 600 spectrophotometer. The ammonia content was now found by comparing the extinction co-:efficient with a calibration value for the reagent previously obtained using ammonium sulphate A.R. (dried). It was found that the extinction coefficient was pro-:portional to the concentration of ammonia over the range used.

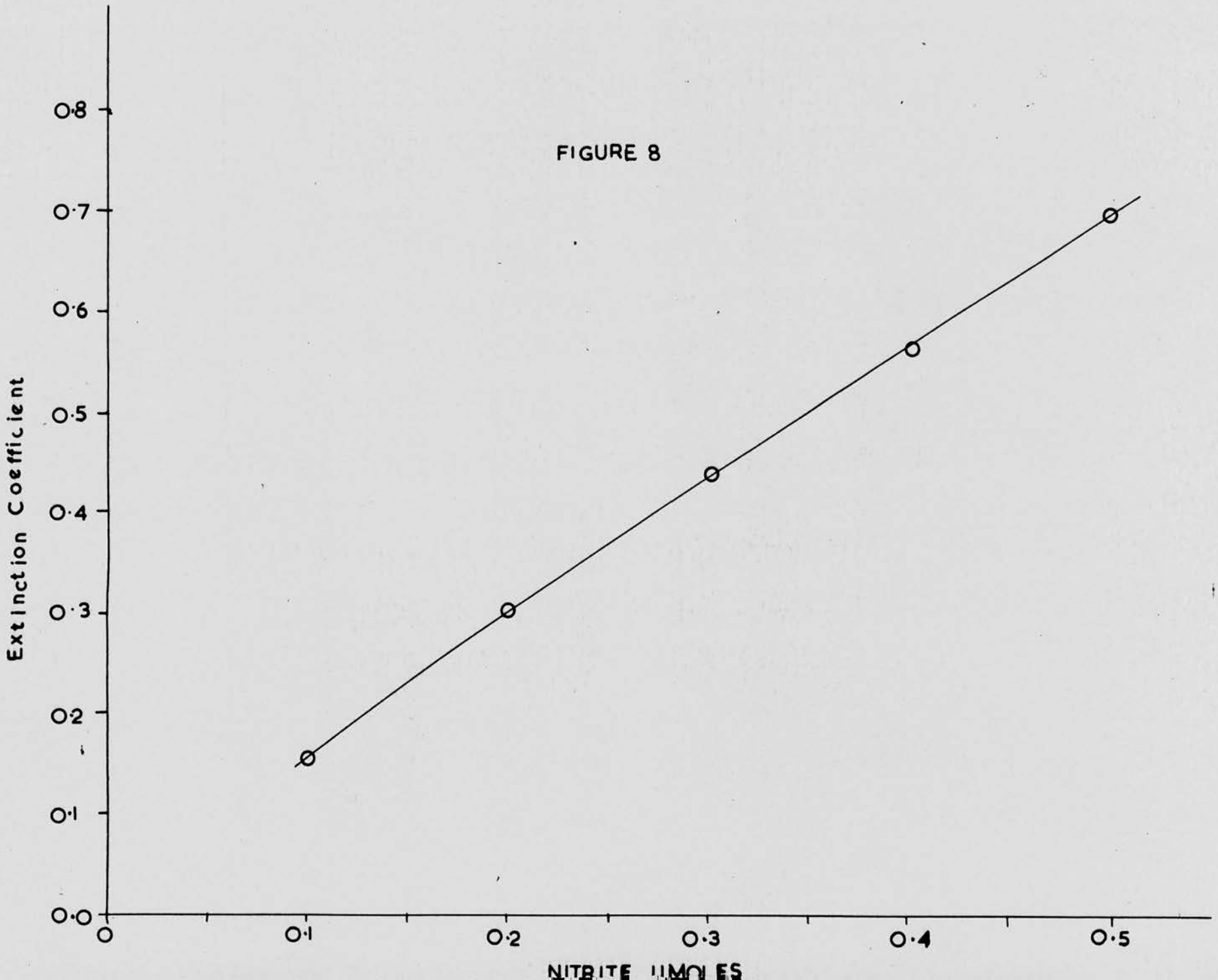
Extinction coefficient = 2.19/μ mole/ml. with a 1 cm. light path.

Estimation of Nitrite

When a zinc oxide film, containing ammonia, which had been illuminated in presence of oxygen, was washed with water, small amounts of nitrite were detected in the washings. This nitrite was estimated as follows.

The washings were made up to 50 ml. with water and a suitable sample (2 to 10 ml.) withdrawn and made up to 20 mls. with water. 2 ml. of Griess-Llosvay reagent, prepared/

FIGURE 8


Extinction Coefficient
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0·0
0
0·1
0·2
0·3
0·4
0·5
NITRITE UMOLES

prepared as on p. (30) were added to this test solution. A blank solution of 20 mls. water and 2 mls. Griess-Llosvay reagent was also prepared and both blank and test solutions were immersed in an 80°C. water bath for 10 mins. during which time a pink colour developed in the test solution when nitrite was present. The solutions were cooled to room temperature and the ex-:tinction coefficient at λ = 520 mμ. of the test solution was measured using the Unicam S.P. 600 spectro-:photometer. By comparing the value obtained with a calibration curve for Griess-Llosvay reagent previously obtained using standard sodium nitrite solution the nitrite content of the test solution was obtained.

Calibration Data for Griess-Llosvay Reagent

Concentration of standard sodium nitrite solution = 0.05 μ moles/ml.

Total volume of test solution = 22 ml.

Volume of standard nitrite in test solution	Nitrite in test solution	Extinction coefficient
2 ml.	0.1 μ moles	0.158 at λ = 520 mμ
4	0.2	0.305
6	0.3	0.442
8	0.4	0.568
10	0.5	0.701

This/

This data is expressed as a calibration curve in figure (8).

Measurement of Intensity of λ = 3650 Å Light

As light of λ = 3650 Å, which accounts for only a small part of the total illumination, causes most of the oxygen uptake observed, (p.106), the intensity of light of this wavelength falling on the zinc oxide film was measured as follows.

25 ml. 0.1M oxalic acid and 25 ml. 0.02M uranyl sulphate, in a glass filter cell of 1 cm. light path, were placed in the position of the reaction flask and illuminated with λ = 3650 Å light from the mercury lamp isolated by means of a 2 mm. Wood's glass filter. After 2 hours illumination the mixture was removed from the filter cell and titrated with 0.2N potassium per-:manganate, light being admitted to the titration flask only as the end point was approached. The experiment was repeated without illuminations and the titre obtained previously was subtracted from the result.

As the beam of light was focused on the position of the zinc oxide film the area of the film was taken as the area of illumination. The transmission ratio was obtained by measuring the light transmitted by the filter cell when filled with uranyl oxalate and again when filled with water, with a barrier type photo cell and/

and galvanometer. The experiment was conducted at 25°C. when the quantum efficiency of the reaction

$$UO_2^{++} + h\nu \rightarrow (UO_2^{++})^*$$

$$(UO_2^{++})^* + (CO_2H)_2 \rightarrow UO_2^{++} + CO_2 + CO + H_2O$$

was 0.49 (36)

Calculation

Normality of $KMnO_4$ solution = 0.1965N

Titrations of $UO_2.SO_4$ and $(CO_2H)_2$ against $KMnO_4$ solution

1) With illumination

25 ml. $(CO_2H)_2 \equiv$ 25.31 ml. $KMnO_4$

repeat 25 ml. $(CO_2H)_2 \equiv$ 25.32 ml. $KMnO_4$

2) Without illumination

25 ml. $(CO_2H) \equiv$ 25.60 ml. $KMnO_4$

repeat 25 ml. $(CO_2H) \equiv$ 25.59 ml. $KMnO_4$

Thus $(CO_2H)_2$ decomposed = 0.28 ml. 0.1965N $KMnO_4$

Molecules of $(CO_2H)_2$ decomposed = $\frac{0.5 \times 0.28 \times 0.1965 \times 6.06 \times 10^{23}}{1000}$

$= 1.668 \times 10^{19}$ molecules

Quantum Efficiency of reaction (φ) = 0.49

Molecules of $(CO_2H)_2$ decomposed if $\varphi = 1$ = $\frac{1.668 \times 10^{19}}{0.49}$

$= 3.403 \times 10^{19}$

Time of illumination = 2 hrs. = 3600 x 2 secs.

Transmission coefficient $\left\{\frac{G_2}{G_1}\right\}$ = 0.698 = $\frac{\text{transmitted light}}{\text{incident light.}}$

Thus $3.403 \times 10^{19} = AIo\,(1-\frac{G_2}{G_1}) \times 2 \times 3600$; A = area of illumination

∴ AIo/

$$\therefore \quad \underline{AIo} = \frac{3.403 \times 10^{19}}{(1 - 0.698) \times 2 \times 3600}$$

$$= \underline{1.564 \times 10^{16} \ h\nu/sec}.$$

$$\underline{A} = \underline{13.8 \ cm^2}$$

$\underline{Io = 1.13 \times 10^{15} \ h\nu/sec/cm^2}$. This being an approximate value.

The intensity of the 3650 Å light is then of the order of 10^{15} $h\nu/sec/cm^2$.

RESULTS and CONCLUSIONS

RESULTS AND CONCLUSIONS

The Photo-uptake of Oxygen

On the addition of oxygen to a prepared film of zinc oxide, no change in pressure in the dark was observed, but on illumination a decrease was immediately noted the rate of pressure decrease becoming less with time. Pressure and time measurements were taken and the oxygen photo-uptake isotherms for a large number of zinc oxide films of various weights in spherical and type IV reaction flasks, were obtained, and fn (R) against fn ($\Sigma\Delta P$) graphs derived from them. All films gave the same types of rate curves; the results of two experiments are given below.

In these experiments, films of 0.1 g. zinc oxide hyperfine were used in order to obtain a substantial pressure decrease, and the runs were continued for 80 and 220 hours respectively. In the first case a type IV flask was used and illumination was by a 250W mercury lamp, while in the second case a spherical flask was used and illumination by a 125W mercury lamp gave a slower uptake.

Since the total pressure decrease was less than 4 mm. during illumination, the initial oxygen pressure of 50 mm. remained effectively constant (see p.92). The following rate curves were derived from the isotherms obtained:-

R/

R against $\Sigma\Delta P$; $^{1}/_{R}$ against $\Sigma\Delta P$

log R against $\Sigma\Delta P$; R against log ($\Sigma\Delta P$).

The results obtained are given in tables (1) and (2) and are shown diagrammatically in figures (9), (10), (11) and (12).

TABLE 1/

Fig. 9a.

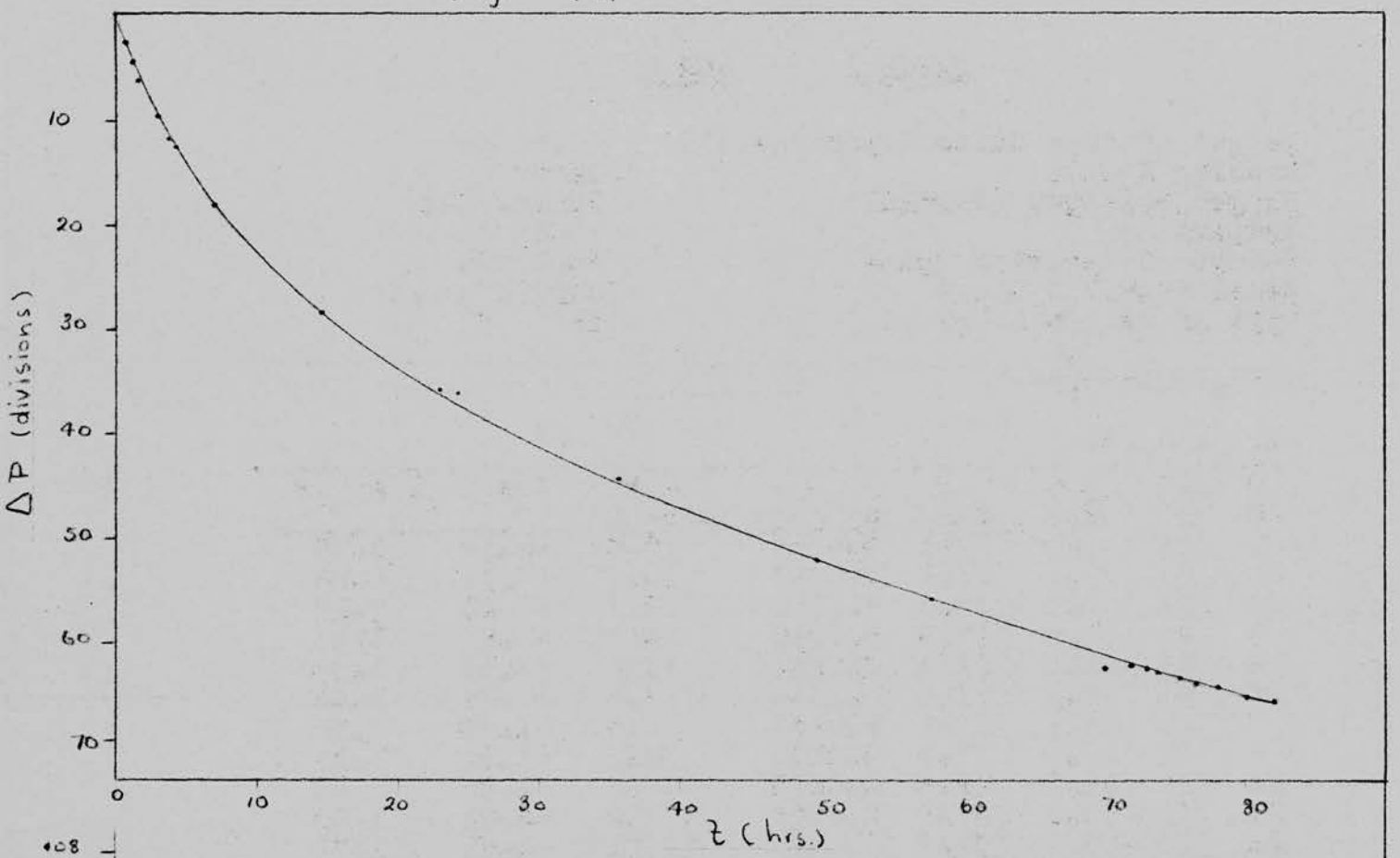

ΔP (divisions)
10
20
30
40
50
60
70
0
10
20
30
40
50
60
70
80
t (hrs.)

Fig. 9b.

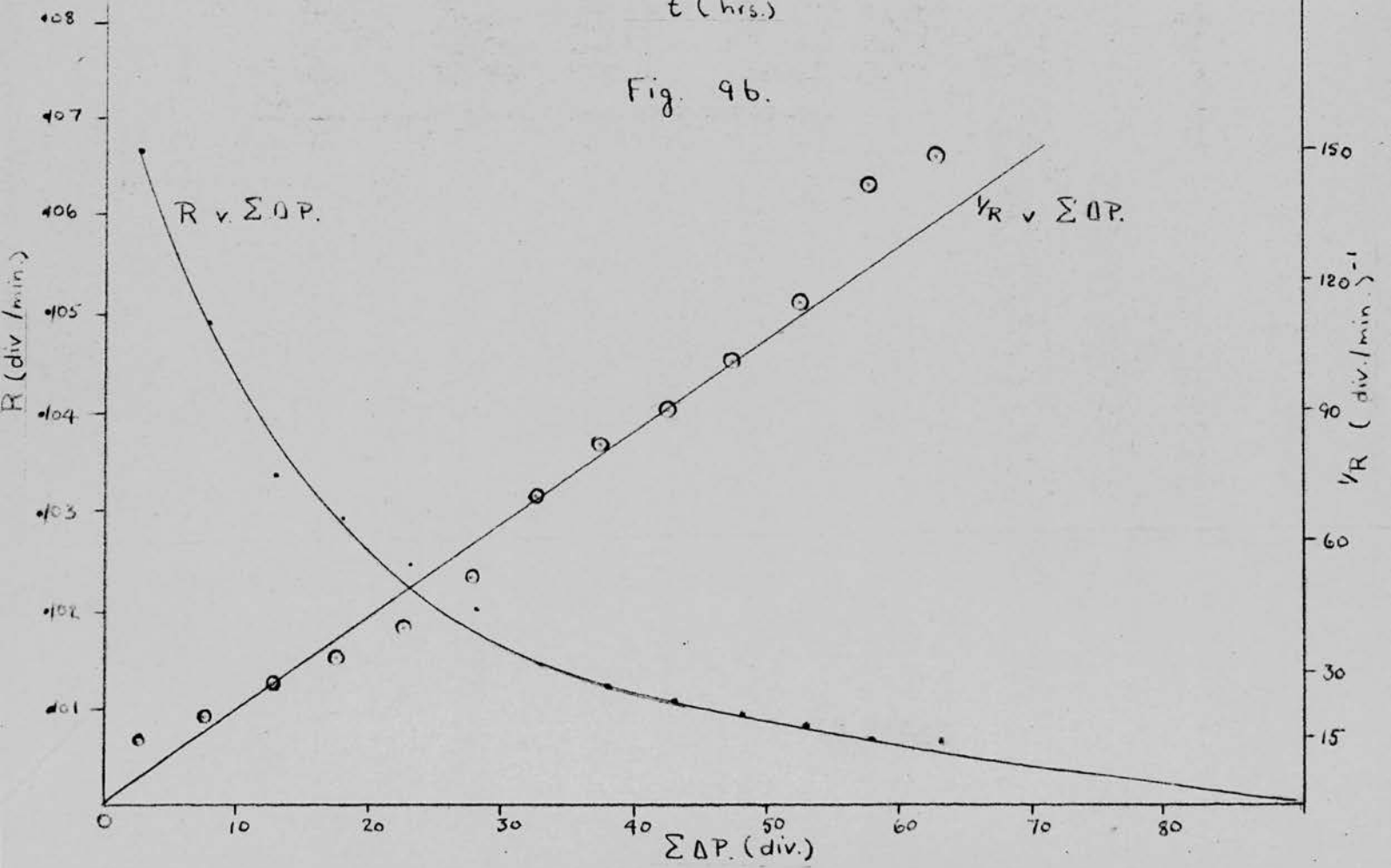

R v. ΣΔP.
1/R v ΣΔP.
R (div/min.)
1/R (div./min.)⁻¹
1.08
1.07
1.06
1.05
1.04
1.03
1.02
1.01
150
120
90
60
30
15
0
10
20
30
40
50
60
70
80
ΣΔP. (div.)

TABLE 1 RUN 1

Weight of Zinc Oxide Hyperfine III = 0.100 g.
Binding Liquid = Water
Oxygen Pressure (Initial) = 50 mm. (Hg)
Temperature = 25.0° C.
Volume of Reaction Space = 60.9 ml.
Sensitivity of Gauge = 0.0552 mm/div.
Type of Reaction Vessel = IV

t hr	t min	ΔP div.	ΣΔP div.	R div/min	1/R min/div	log R	log ΣΔP
0	00	0.0					
0	37	2.7					
1	03	4.7	2.5	0.0668	15.0	-1.18	0.40
1	36	6.6	7.5	0.0490	20.4	-1.31	0.88
2	54	9.8	12.5	0.0354	28.2	-1.45	1.10
3	42	11.9	17.5	0.0292	34.2	-1.53	1.24
4	13	12.7	22.5	0.0244	41.0	-1.60	1.35
5	04	14.8	27.5	0.0190	52.6	-1.72	1.44
5	20	15.3	32.5	0.0140	71.5	-1.85	1.51
6	53	18.1	37.5	0.0120	83.3	-1.92	1.57
14	25	28.7	42.5	0.0110	91.4	-1.96	1.63
23	00	35.8	47.5	0.0098	102.0	-2.01	1.68
24	20	36.2	52.5	0.0086	116.1	-2.07	1.72
35	35	44.7	57.5	0.0070	143.0	-2.16	1.76
49	40	52.5	62.5	0.0067	150.0	-2.18	1.80
57	25	56.7					
70	00	62.4					
71	40	62.6					
73	00	62.9					
73	40	63.0					
75	15	63.9					
75	50	64.0					
76	30	64.5					
77	10	64.6					
77	50	64.7					
78	10	64.8					
80	00	65.7					
80	30	65.5					
81	15	65.8					
82	00	65.9					

TABLE 2/

Fig. 10 a.

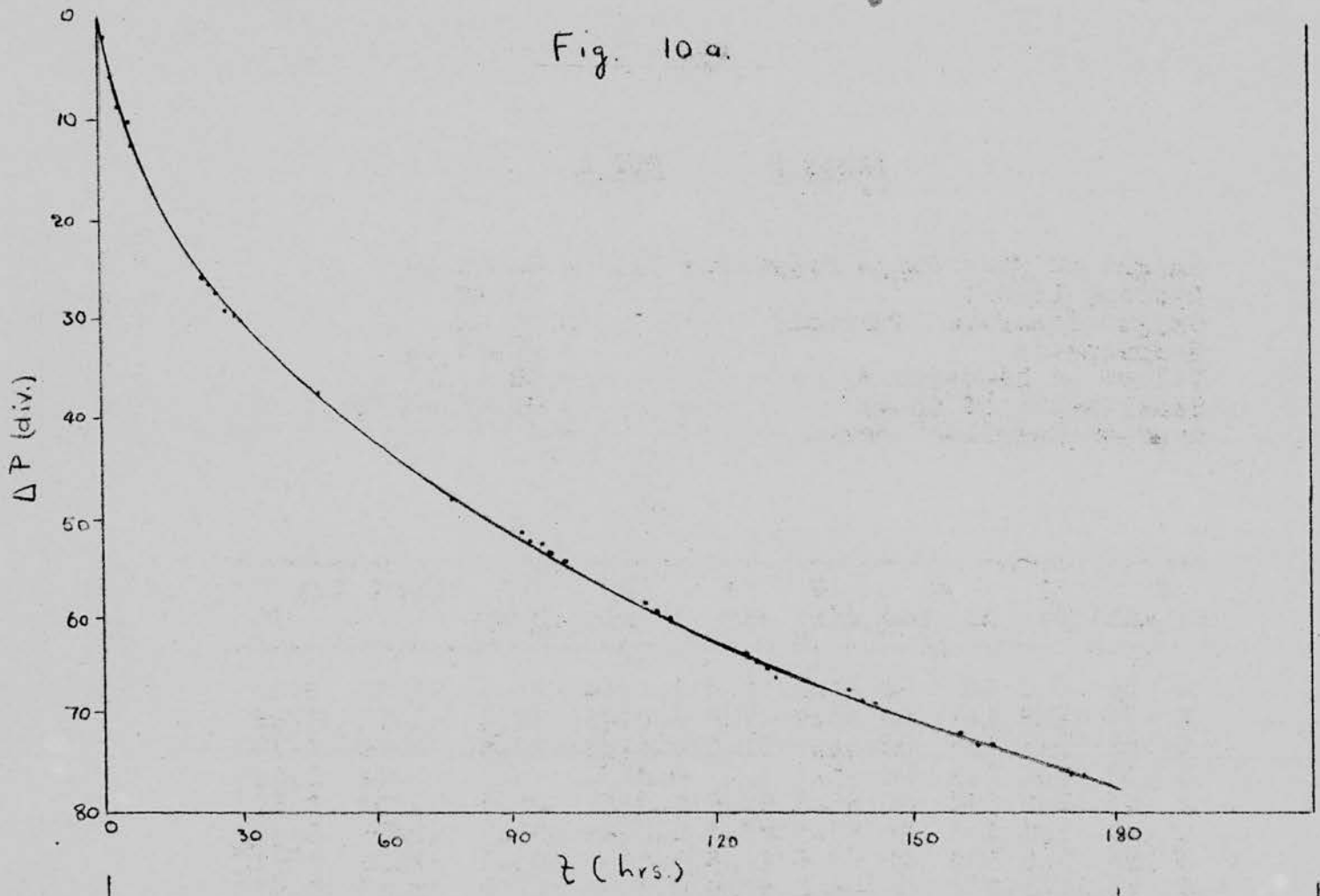


Fig. 10 b.

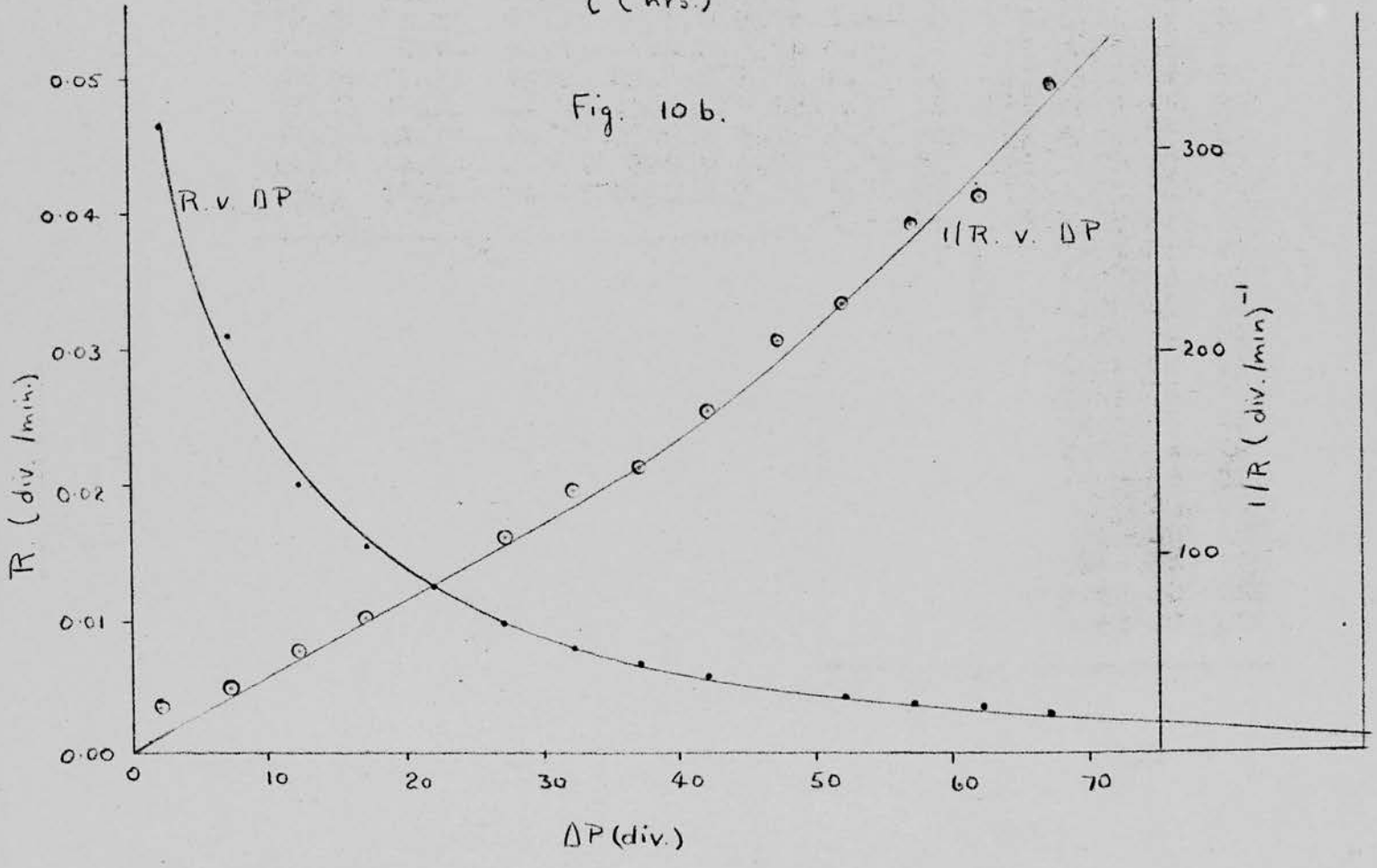


TABLE 2 RUN 2

Weight of Zinc Oxide Hyperfine III = 0.100 g.
Binding Liquid = Water
Oxygen Pressure (Initial) = 50 mm.
Temperature = 25.0° C.
Volume of Reaction Space = 48.4 ml.
Sensitivity of Gauge = 0.023 mm/div.
Type of Reaction Vessel = I

t hr	t min	ΔP div.	t hr.	t min	ΔP div.	ΣΔP div.	R div/min	1/R min/div	log R	log (ΣΔP)
0	00	0.0	126	00	60.1	2.5	0.0464	21.6	-1.33	0.40
0	37	2.2	144	00	63.9	7.5	0.0308	32.4	-1.51	0.88
0	51	3.1	146	00	64.6	12.5	0.0198	50.5	-1.70	1.10
1	36	5.1	148	00	65.3	17.5	0.0151	66.2	-1.82	1.24
2	07	6.2	150	00	66.2	22.5	0.0121	82.5	-1.92	1.35
2	40	7.2	167	20	67.5	27.5	0.0094	106.3	-2.03	1.44
3	56	9.0	170	00	68.6	32.5	0.0077	130.0	-2.11	1.51
6	11	12.1	172	00	68.6	37.5	0.0068	147.0	-2.17	1.57
6	50	13.0	174	10	69.0	42.5	0.0059	169.4	-2.23	1.63
7	25	13.5	190	30	71.8	47.5	0.0049	204.0	-2.31	1.68
22	48	26.2	193	20	72.5	52.5	0.0044	227.0	-2.36	1.72
23	30	26.8	196	00	73.1	57.5	0.0038	263.0	-2.42	1.76
25	00	27.1	198	00	72.6	62.5	0.0036	278.0	-2.44	1.80
25	35	28.0	217	00	76.3	67.5	0.0030	334.0	-2.52	1.83
27	55	29.5	217	45	76.2					
28	30	29.5								
30	10	30.3								
31	00	30.6								
48	45	38.0								
49	30	38.1								
77	45	48.5								
94	30	51.8								
95	43	52.5								
98	00	52.9								
100	00	53.8								
101	20	54.5								
102	45	54.8								
120	05	58.5								
124	00	59.6								

It/

Fig. 11

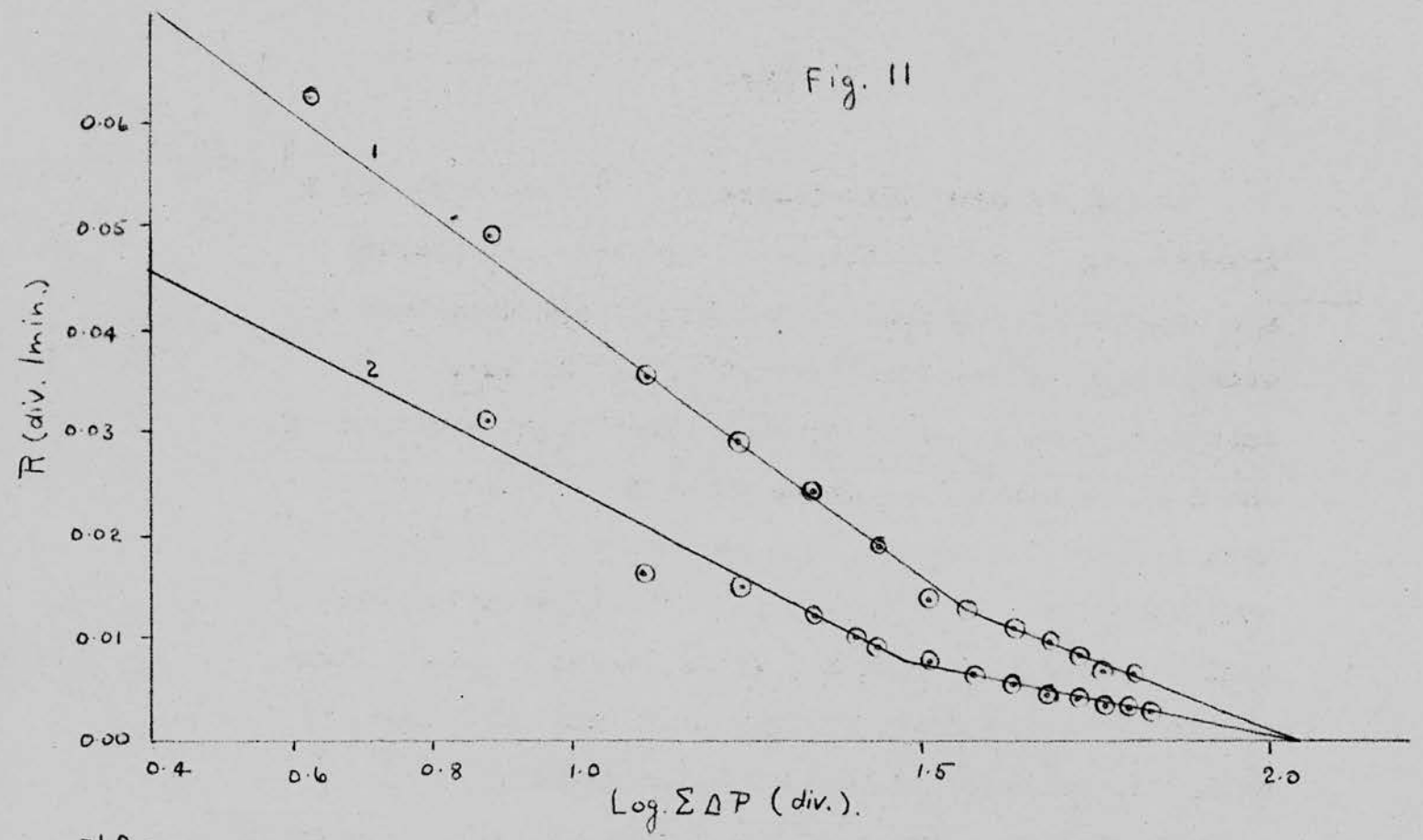
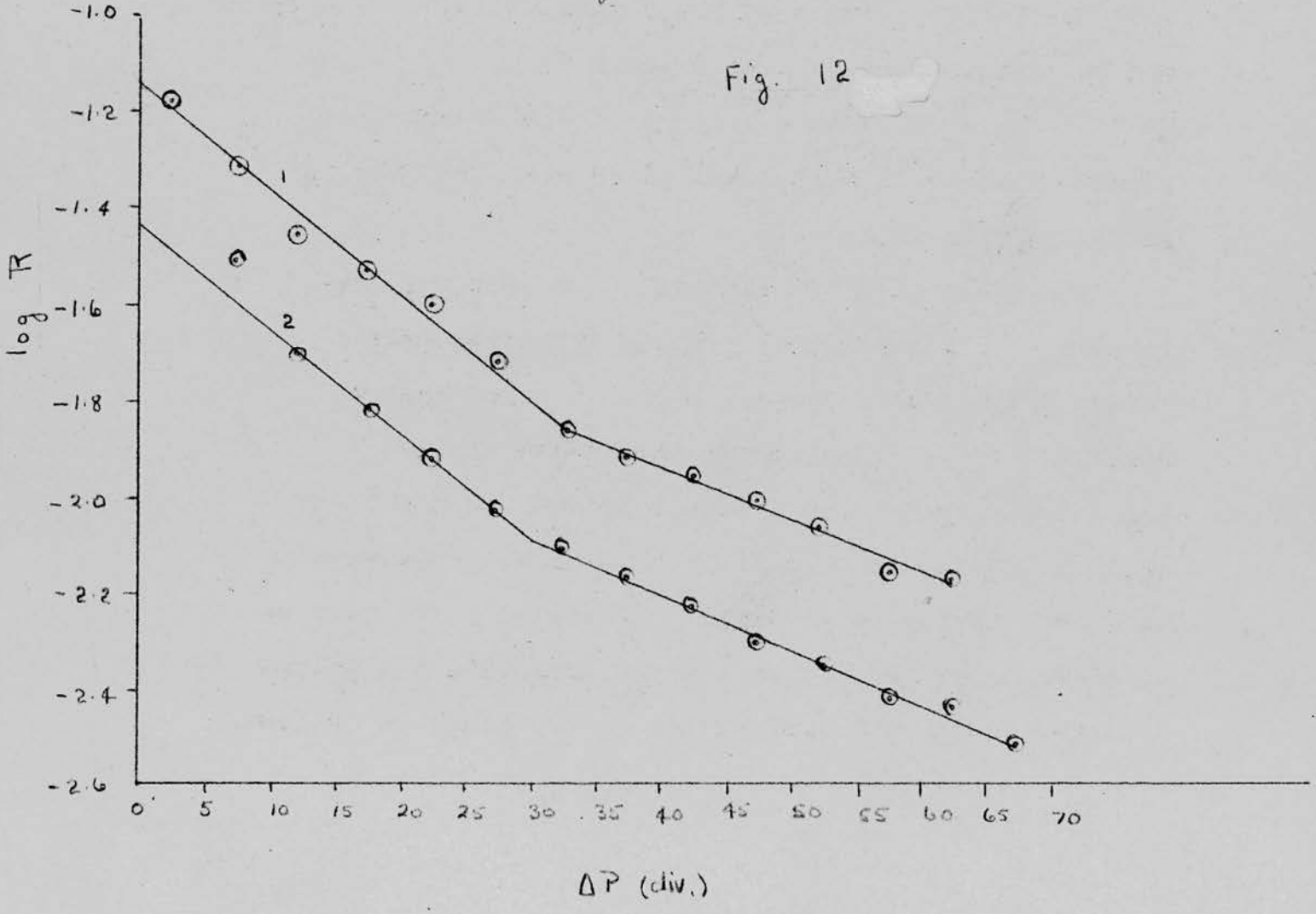

0·06
0·05
0·04
0·03
0·02
0·01
0·00
R (div. /min.)
1
2
0·4
0·6
0·8
1·0
1·5
2·0
Log. ΣΔP (div.).

Fig. 12


-1·0
-1·2
-1·4
-1·6
-1·8
-2·0
-2·2
-2·4
-2·6
log R
1
2
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
ΔP (div.)

It can be seen from figures (11, 12) that both the R against log ($\Sigma\Delta P$) and the log R against $\Sigma\Delta P$ graphs are apparently composed of two linear portions with a sharp break between them occurring at the same $\Sigma\Delta P$ value for both types of graph. The linear portions of the log R against $\Sigma\Delta P$ graph gives an equation of the type derived by Roginsky and Zeldovich [37] for chemisorption. For some types of chemisorption the Roginsky-Zeldovich equation gives broken straight lines, similar to those found in this work, and have been explained in terms of surface heterogeneity[38].

The latter portion of the R against log $\Sigma\Delta P$ graph can be extrapolated to give a value for $\Sigma\Delta P_\infty$ (i.e. $\Sigma\Delta P$ at $R = 0$ which is a measure of the pressure decrease which will have taken place when the film is saturated with oxygen.

The slope of the R against $\Sigma\Delta P$ graph (figures 9b, 10b) is seen to diminish rapidly until an approximately linear relationship between R and $\Sigma\Delta P$ is observed, starting in the region where the breaks in the logarithmic graphs occur (about 35 div. in run 1 and about 30 div. in run 2). If this curve is assumed to be linear in its later stages a value of $\Sigma\Delta P_\infty$ can be obtained by extrapolation and compares with the values obtained from the R against log ($\Sigma\Delta P$) graph as follows.

Run 1/

	Run 1	Run 2
$\Sigma\Delta P_\infty$ from R against $\Sigma\Delta P$ graph	= 92 div.	100 div.
$\Sigma\Delta P_\infty$ from R against log $(\Sigma\Delta P)$ graph	= 109 div.	111 div.

It is apparent that although of the same order the values obtained by using the logarithmic graphs are larger (9%) than those obtained using the R against $\Sigma\Delta P$ graph. The appearance of the latter curve suggests that the straight line drawn through the later points is not altogether justified and the value of $\Sigma\Delta P_\infty$ obtained using the former will be the better approxi-:mation. Extrapolated values of $\Sigma\Delta P_\infty$ were therefore determined by this method.

The values of $\Sigma\Delta P_\infty$ obtained were assumed to be valid only for the comparison of oxygen uptakes on different films.

The $^1/R$ against $\Sigma\Delta P$ curves shown in figure (9b, 10b) are approximately linear in their initial stages and a straight line has been drawn through the origin in accordance with a parabolic type of ΔP against t curve. The equation of the linear portion of this rate curve can be expressed as

$$^1/R = m\Delta P + C$$

and as $R = \frac{d\Delta P}{dt}$, $\frac{dt}{d(\Delta P)} = m\Delta P + C$ where m is the slope of the line and C is the intercept on the $^1/R$ axis

$$dt = m\Delta P.dP + C d\Delta P$$

$$\therefore t = \frac{m}{2}\Delta P^2 + C\Delta P + K, \text{ where K is a}$$

constant,/

constant, and as $t = 0$ at $\Delta P = 0$, $K = 0$

$$\therefore t = \frac{m}{2}\Delta P^2 + C\Delta P = \frac{m}{2}(\Delta P + P)^2 + K^1$$

where $P = \frac{c}{m}$ and K^1 is a constant

Values of t and $(\Delta P + P)^2$ obtained experimentally in runs 1 and 2 are given in table 3 together with values obtained during oxygen uptake by a film of 0.04g. zinc oxide hyperfine III run 3 which was bound with acetone, and are shown diagrammatically in figure (13).

While the value of P for runs 1 and 2 was taken as zero, in the case of the acetone bound film P was found to be -0.6.

The linear nature of the $(\Delta P + P)^2$ curves demonstrate the parabolic nature of the oxygen uptakes with respect to time.

TABLE 3/

Fig. 13

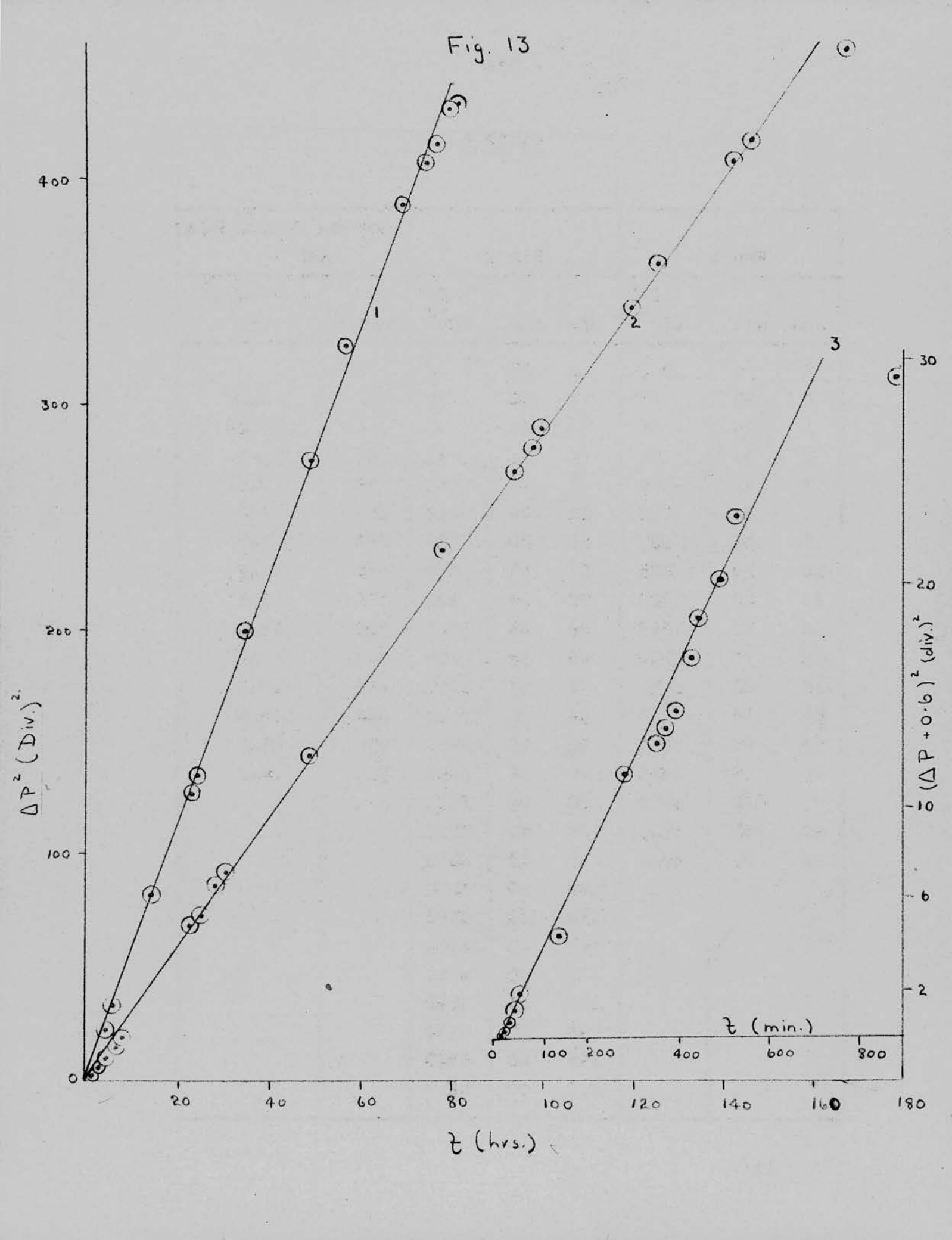

400
300
200
100
0
ΔP² (Div.)²
1
2
3
20
40
60
80
100
120
140
160
180
t (hrs.)
0
100
200
400
600
800
t (min.)
30
20
10
6
2
(ΔP + 0·6)² (div.)²

TABLE 3

Run 1			Run 2			Acetone Bound Film Run 3	
t hrs.	t min.	$(\Delta P)^2$ div^2	t hrs.	t min.	$(\Delta P)^2$ div^2	t min.	$(\Delta P-0.6)^2$ $(div)^2$
0	0	0.0	0	00	0	0	
0	55	16	2	40	52	23	0.25
1	29	36	3	56	81	34	0.49
2	54	96	6	11	146	47	1.0
3	42	161	7	25	182	55	1.9
5	04	219	22	48	688	138	4.4
6	58	327	25	00	734	280	11.6
14	25	825	27	55	870	350	12.9
23	00	1280	30	10	920	375	13.6
24	52	1355	48	45	1440	390	14.4
35	35	2000	49	30	1450	430	16.8
49	40	2751	77	45	2350	445	18.5
57	25	3270	94	30	2690	490	20.3
70	00	3890	98	00	2800	530	23.0
75	15	4080	100	00	2890	890	29.2
77	10	4170	120	05	3420		
80	00	4320	126	00	3620		
82	00	4340	143	25	4070		
			146	00	4170		
			150	00	4380		
			167	20	4560		
			172	00	4710		
			175	15	4840		
			190	30	5170		
			196	00	5340		
			217	00	5810		

It/

It therefore appears that the oxygen uptake is approximately parabolic in its initial stages, tending towards an exponential type of curve as the illumination continues. This is very similar to the oxygen uptake of the rutile form of titanium dioxide (Kennedy[6]), the main difference between the oxides being the much greater extent to which titanium dioxide will take up oxygen compared with zinc oxide.

As the uptake is approximately parabolic it might be expected that the R against log $\Sigma\Delta P$ graph would be a curve. It is considered, however, that any error incurred by interpreting it linearly can be neglected so far as interpolation of rates in the relative rate method (p. 38), as comparison of uptakes of films of the same weight are concerned.

Preliminary experiments were carried out to determine whether the oxygen uptake was a reversible or a non-reversible process and these are now described.

Experiments on Reversibility of Oxygen Uptake

Experiments were carried out to determine whether any desorption of oxygen took place, (a) when illumination of a film of zinc oxide in oxygen was interrupted, or (b) when a film which had taken up oxygen, was allowed to stand in vacuo, either with illumination, or in the dark.

In/

In the latter two cases, films which had taken up oxygen were quickly evacuated to 10^{-3} mm. (5-10 min) and left overnight either in darkness or with illumina-:tion. In no case was any pressure change detectable with the Bourdon gauge (0.018 μ moles) observed.

In the former case, experiments with acetone, and water, bound films gave similar results, when illumina-:tion was interrupted for periods of 16 hrs. Rate curves were constructed from the isotherms obtained and compared with rate curves obtained during continuous illumination. The results of two typical experiments are now given.

TABLE 4/

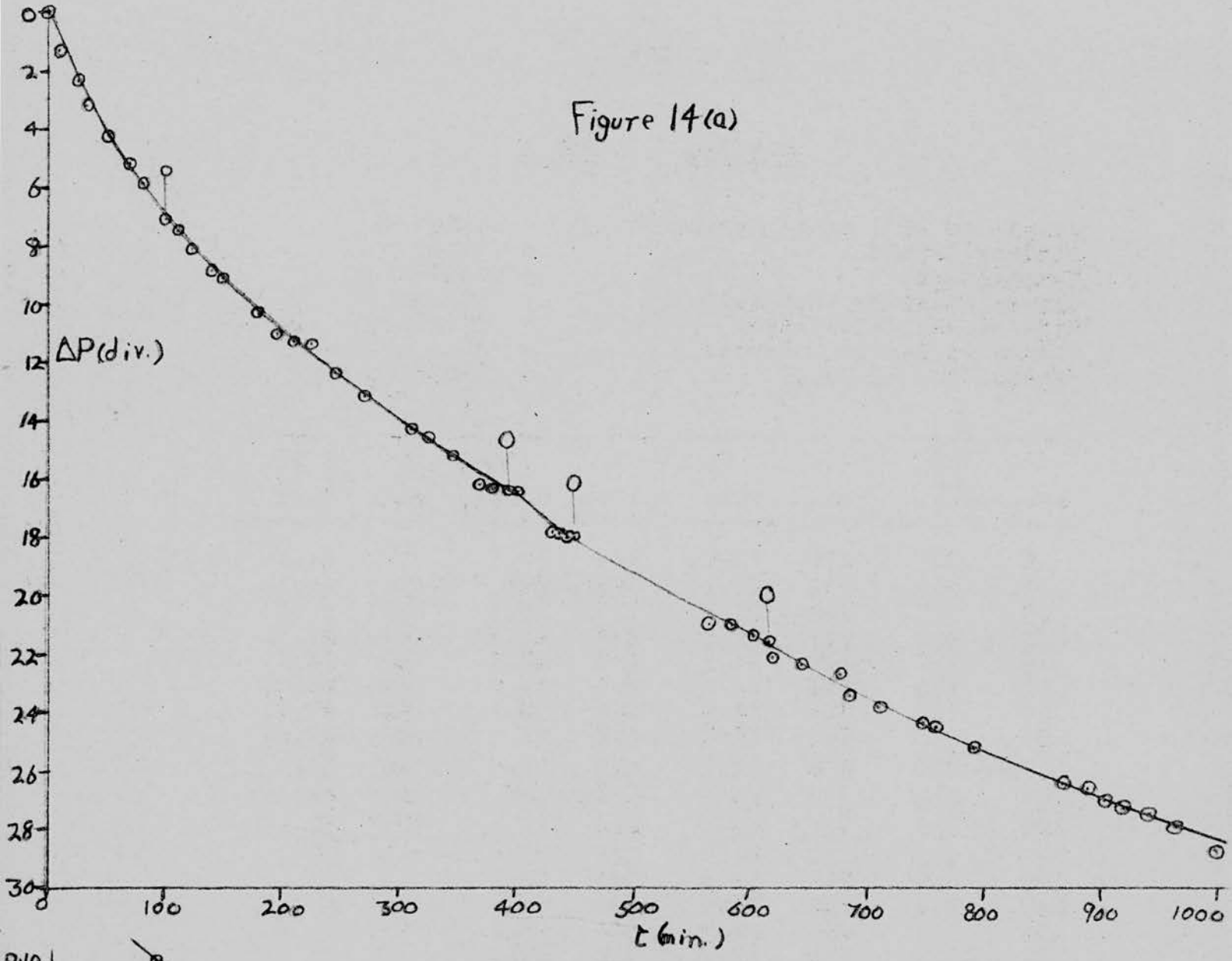


Figure 14(a)

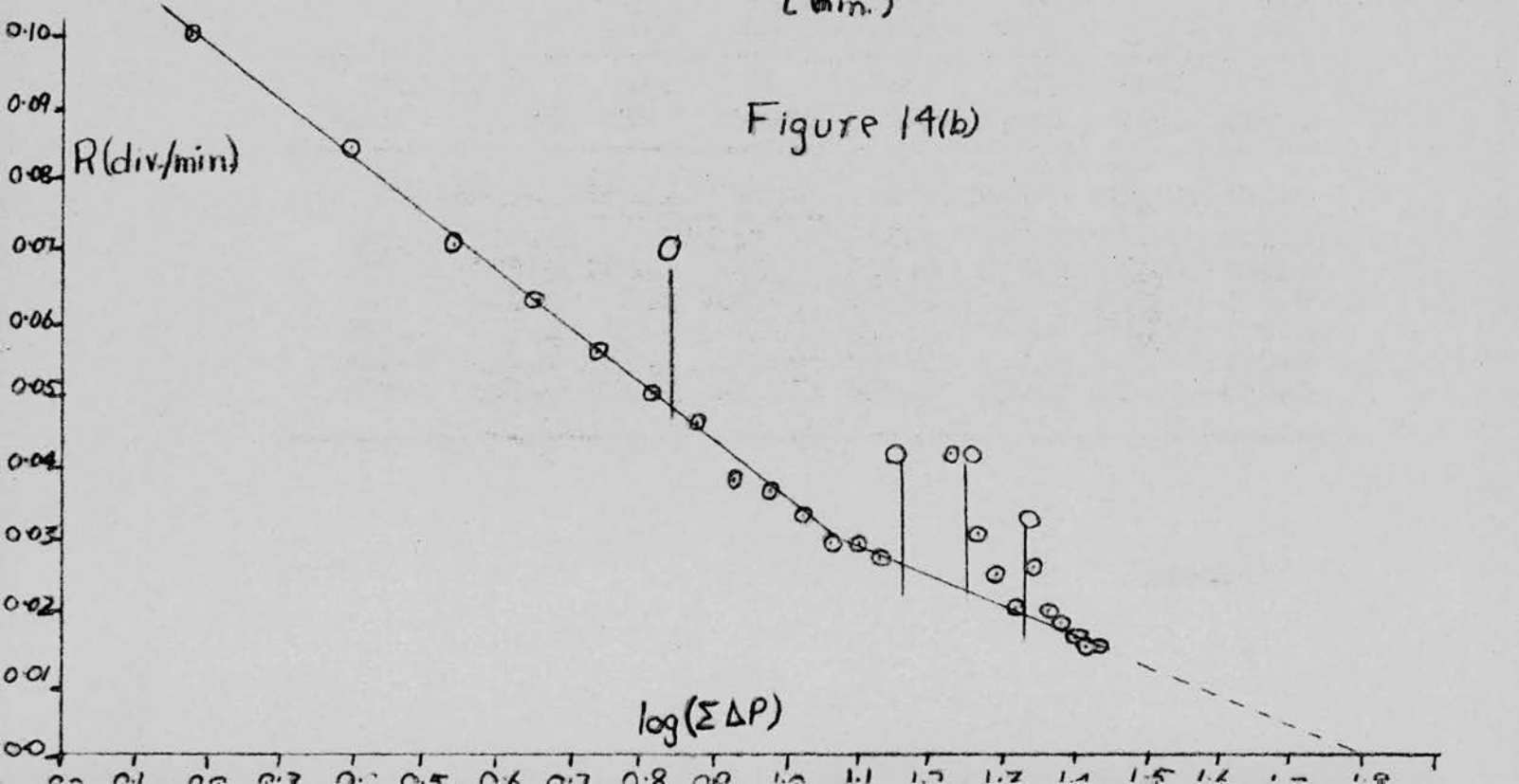


Figure 14(b)

TABLE 4 RUN 4

Weight of Zinc Oxide Hyperfine III = 0.100 g.
Binding Liquid = Water
Temperature = 25.0° C.
Oxygen Pressure (Initial) = 50 mm.
Type of Reaction Vessel = IV silica
Volume of Reaction Vessel = 60.4 ml.
Sensitivity of Gauge = 0.055 mm/div.

t min.	ΔP div.	t min.	ΔP div.	t min.	ΔP div.	t min.	ΔP div.
0	0.0	196	11.0	435	17.7	747	24.3
10	1.3	209	11.2	OVERNIGHT		759	24.4
25	2.3	222	11.3	435	17.7	790	25.2
32	3.2	243	12.3	443	17.9	868	26.3
49	4.2	269	13.1	450	17.9	889	26.5
67	5.2	310	14.2	564	20.8	903	26.9
80	5.8	326	14.5	585	20.9	917	27.1
99	7.1	346	15.2	602	21.3	939	27.4
OVERNIGHT		368	16.1	612	21.5	963	27.8
99	7.1	378	16.2	OVERNIGHT		997	28.6
109	7.5	383	16.3	612	21.5	1037	30.2
121	8.1	30 MIN.		621	22.0		
139	8.8	383	16.3	643	22.3		
149	9.1	390	16.3	674	22.6		
154	9.2	400	16.3	684	23.4		
177	10.2	431	17.7	711	23.7		

R div/min	log (ΣΔPdiv)	R div/min	log (ΣΔPdiv)	R div/min	log (ΣΔPdiv)	R div/min	log (ΣΔP div)
0.125	-0.300	OVERNIGHT		0.027	1.130	OVERNIGHT	
0.100	0.176	0.046	0.875	30 MIN		0.026	1.342
0.084	0.398	0.038	0.929	0.042	1.231	0.020	1.362
0.071	0.544	0.037	0.978	OVERNIGHT		0.018	1.380
0.063	0.653	0.033	1.021	0.030	1.267	0.016	1.398
0.056	0.740	0.029	1.062	0.025	1.290	0.015	1.414
0.050	0.812	0.029	1.098	0.020	1.312	0.015	1.431

These/

These results are shown diagrammatically in figures (14a and b). The R against log $\Sigma\Delta P$ curve (figure 14b) is of the form obtained with continuous illumination of films of this weight using the same type of reaction flask (p.50).

This experiment was also carried out using a film of 0.02 g. zinc oxide; the results obtained are given in table (5) and are shown in figures (15a and b).

TABLE 5/

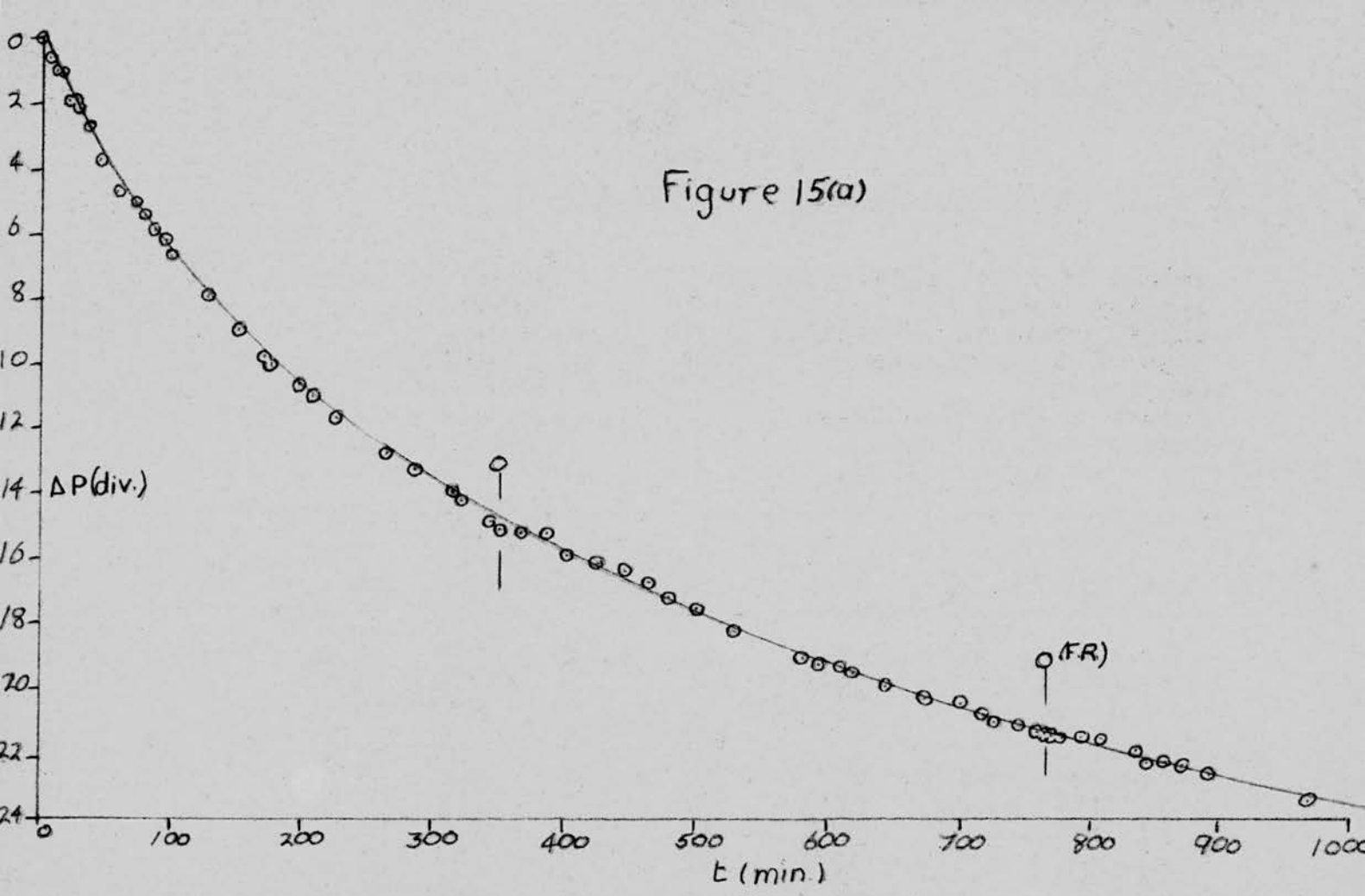


Figure 15(a)

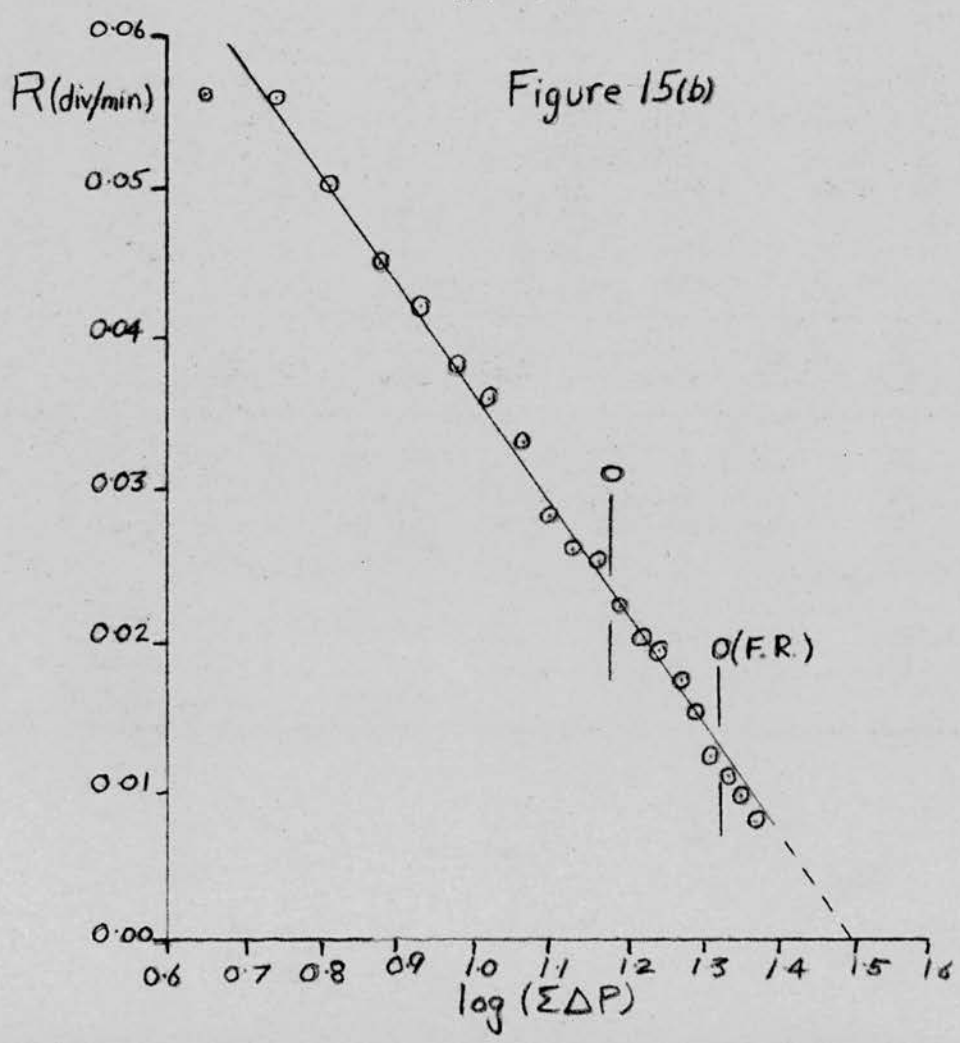


Figure 15(b)

TABLE 5 RUN 5

Weight of Zinc Oxide Hyperfine III = 0.019 g.
Binding Liquid = Water
Oxygen Pressure (Initial) = 50 mm.
Type of Reaction Vessel = IV silica
Temperature = 25.8° C.
Volume of Reaction Vessel = 60.4 ml.
Sensitivity of Gauge = 0.055 (div/mm.)$^{-1}$

t min.	ΔP div.	t min.	ΔP div.	t min.	ΔP div.	t min.	ΔP div.
0	0.0	150	8.9	422	16.0	765	21.3
7	0.7	169	9.8	446	16.3	OVERNIGHT FILM REVERSED	
				463	16.7		
10	1.0	175	10.1	480	17.2	765	21.3
14	1.1	197	10.6	500	17.5	770	21.3
19	1.9	224	11.6	527	18.1	775	21.4
24	2.0	262	12.7	578	19.0	780	21.5
28	2.2	286	13.2	593	19.2	795	21.5
35	2.8	314	13.9	609	19.3	809	21.5
44	3.8	320	14.1	618	19.5	835	21.9
59	4.7	342	14.8	642	19.9	845	22.2
72	5.1	350	15.0	674	20.2	859	22.2
78	5.5	OVERNIGHT		701	20.3	870	22.3
86	5.9	350	15.0	718	20.7	891	22.6
94	6.2	365	15.1	725	21.0	987	23.4
100	6.7	384	15.2	745	21.1	1115	24.4
126	7.9	400	15.8	759	21.3	1130	24.6

R div/min	log (ΔP div)	R div/min	log (ΔP div)	R div/min	log (ΔP div)	R div/min	log (ΔP div)
0.091	-0.301	0.050	0.81	0.028	1.10	0.017	1.27
0.083	0.18	0.045	0.88	0.026	1.13	0.015	1.29
0.077	0.40	0.042	0.93	0.025	1.16	0.012	1.31
0.071	0.59	0.038	0.98	OVERNIGHT		OVERNIGHT FILM REVERSED	
0.056	0.65	0.036	1.02	0.022	1.19	0.011	1.33
0.056	0.74	0.033	1.06	0.020	1.22	0.0095	1.35
				0.019	1.24	0.008	1.37

In/

In this case, it can be seen (Figure 15b) that the R against log $\Sigma\Delta P$ graph is a good straight line throughout the run, and no break appears in the graph when illumination has been interrupted. When the film was reversed and illuminated from the reverse side little change was apparent in the rate plot.

It was concluded that, for a film of low weight (0.02 g.), interrupting the illumination does not affect the rate of the subsequent reaction, except at low rates (0.01 div/min) when temporary increases in rate were observed for some samples. For films of 0.1 g. weight, interrupting the illumination in the early stages of the reaction does not affect the rate of the subsequent reaction, but in later stages of the reaction interruption of illumination caused an increased rate when illumination was recommenced, which was only temporary the rates rapidly falling back to the original R against log $\Sigma\Delta P$ graph. This was taken to indicate that interrupting the illumination does not interfere with the fundamental process of photo-sorption of oxygen in its early stages, the photo-adsorption of oxygen being apparently irreversible.

When a film of zinc oxide is illuminated in vacuo, after the usual evacuation, a slight rise in pressure is noted, in the region of 0.11 mm. in 60 ml. during 24 hrs. for a 0.10 g. film. The gas evolved did not condense/

condense at liquid oxygen temperature. When a film of the same weight which had been illuminated in 50 mm. of oxygen was evacuated for a short time (10 min.) and subsequently illuminated in vacuo for 24 hrs. no change in pressure was observed. It was concluded therefore that the gas evolved by the fresh film was not oxygen but probably nitrogen, hydrogen or carbon monoxide.

PRODUCTS OF PHOTOSORPTION OF OXYGEN

When a film of zinc oxide hyperfine was illuminated in oxygen, water and carbon dioxide were detected in the gas phase. These are the substances that are desorbed during the evacuation of a film prior to a run and it might be considered that this desorption would continue in an atmosphere of oxygen.

The extent of the desorption of these substances during the preliminary evacuation of a film and during illumination in oxygen were investigated and the effect of an atmosphere of oxygen on the dark desorption studied.

Evolution of Water and Carbon Dioxide from Zinc Oxide Hyperfine films.

Water Bound Films

During the preliminary evacuation of a water bound film, water and carbon dioxide are evolved, in different amounts, which decrease as pumping continues.

The rates of evolution of these gases ~~was~~ were measured on a day to day basis by pumping the film at 10^{-4} mm. through a cold trap at liquid oxygen temperature for about 12 hours and allowing it to remain in contact with the cold trap for a further 12 hours. The contents of the cold trap were identified and measured at the end of that/

that time, as on page (39). Large amounts of water and carbon dioxide were obtained during the first three days the rate falling rapidly after that time to an almost steady value. Rates of evolution of water and carbon dioxide at intervals of several days are given below in table 6; the film was treated with oxygen between the measurements given; this being discussed later.

TABLE 6

Film Weight 0.100 g.

Days since start of evacuation	Rate of evolution of water μmoles/hr./g.	Rate of evolution of CO_2 μmoles/hr./g.
Average of 6th & 7th days	0.79	0.11
10th day	0.52	0.072
15th day	0.56	0.11

As the rate of evolution of these gases is still appreciable after long evacuation, it is important to determine the effect of oxygen in the dark, in order to decide whether water and carbon dioxide obtained by pumping the gas phase from an illuminated film through a cold trap are the result of a photo or a thermal process.

During illumination the film stands in an atmos-:phere of gas for several days, thus the effect of standing/

standing evacuated, but with no pumping or contact with a cold surface, and the effects of standing in 50 mm. of oxygen for both short and long periods, on the rate of evolution of water and carbon dioxide were investi-:gated.

Standing without pumping

After several days preliminary evacuation, the rate of evolution of water and carbon dioxide was determined over 2 days as described above and the film, attached to the Bourdon gauge was then sealed off from the rest of the apparatus. No pressure increase detectable by the gauge took place during two days and the film was then pumped through a cold trap for 12 hours and stood in contact with the cold trap for a further 12 hours. The rates of evolution of water and carbon dioxide were calculated for the 24 hours and also the average value for the 3 days. The film was evacuated for the following day and the rates again calculated. It was found that although no pressure increase occurred during 2 days standing the average rates over these 2 days and the following day was similar to the rate expected for continuous evacuation.

Film Weight = 0.100 g.

Average rates for 2 days continuous evacuation
= 1.25 μmoles/hr./g. H_2O and 0.23 μmoles/hr./g. CO_2

Average/

Average rate for 2 days standing and the following days evacuation = 0.79 μmoles/hr./g. H_2O and 0.15 μmoles/hr./g. CO_2

Average rate for 2 days following previous period = 0.50 μmoles/hr./g. H_2O and 0.07 μmoles/hr./g. CO_2

It would thus appear that an "ageing" process is occurring, in which water and carbon dioxide are becoming continuously available for desorption at low pressure (< 0.05 mm.).

Standing in Oxygen in the Dark

The rate of evolution of water and carbon dioxide in vacuo was determined for the zinc oxide film over several days. 50 mm. of oxygen were then admitted and the film was allowed to stand for 9 hours. The oxygen was then quickly pumped out through a liquid oxygen cold trap, the pressure falling to about 0.1 mm. in 2 to 3 minutes. The condensable gases collected in the cold trap were identified as carbon dioxide and water and the rates of evolution were calculated. The film was then pumped to 10^{-4} mm. through the cold trap and was allowed to stand over the cold trap for 12 hours. The rates of evolution of the gases over this period was obtained. 50 mm. of oxygen were again admitted to the film and the above procedure repeated. The film was now pumped for 12 hours and allowed to stand in contact/

contact with a cold trap for a further 12 hours, the rates of evolution of gases over this period being calculated for comparison with those measured in the presence of oxygen. 50 mm. of oxygen were again admitted and allowed to remain in contact with the film for 72 hours. The gases were then pumped through a cold trap and the film allowed to stand in contact with the cold trap for 22 hours the rates of evolution of the gases being measured in both cases, as before. Finally the rates of evolution of the gases in vacuo were again measured during 24 hours.

The results obtained are shown in table 7. No pressure increase took place during standing in 50 mm. O_2 in the dark.

TABLE 7/

T A B L E 7

	Water μmoles/hr./g.	Average Water μmoles/hr./g.	Carbon Dioxide μmoles/hr./g.	Average CO_2 μmoles/hr./g.
Rates over 2 days in vacuo after 5 days preliminary pumping	0.79	0.79	0.11	0.11
Rates over 9 hrs. in 50 mm. O_2	0.215	0.52	0.11	0.13
Rates over 10 hrs. in vacuo	0.63		0.14	
Rates over 10 hrs. in 50 mm. O_2	0.22	0.45	0.09	0.11
Rates over 12 hrs. in vacuo	0.57		0.13	
Rates over 24 hrs. in vacuo	0.50	0.50	0.07	0.07
Rates over 70 hrs. in O_2	0.20	0.32	0.04	0.04
Rates over 22 hrs. in vacuo	0.66		0.07	
Rates over 16 hrs. in vacuo	0.56	0.56	0.11	0.11

From the average rate columns in the above table, it can be seen that only in the case of long standing in oxygen do the average rates/hr. fall much below those obtained in vacuo. From the other columns it is clear that the rates during treatment with oxygen are much lower than the average values in vacuo in the case of water and in the case of carbon dioxide on prolonged treatment with oxygen. The high rates obtained immediately after oxygen treatment in the case of water would indicate that the ageing process has not been affected, the high rates during the last evacuation supporting this. It can also be seen that the rate of water evolution is the same for both long and short periods of oxygen treatment, while the evolution of carbon dioxide is considerably less during prolonged oxygen treatment than during the short oxygen treatments.

The film had been evacuated for five days previous to these experiments and these results were thus obtained during the period in which a film is normally illuminated. These results can therefore be compared with the average rates of appearance of water and carbon dioxide in the gas phase during illumination in O_2. The gas phase was rapidly pumped out through a cold trap and the water and carbon dioxide collected as in the experiments on oxygen treatment above. The amounts of water and carbon dioxide obtained were

divided/

divided by the period of illumination in hours to give the average rate. Typical results for films illumina-:ted in 50 mm. of oxygen are given below.

Film Weight	Time of illumination	Average Rate for H_2O	Average Rate for CO_2
0.10 g.	120 hrs.	0.047 μmoles/hr./g.	0.11 μmoles/hr./g.
0.10 g.	320 hrs.	0.18	0.08
0.10 g.	82 hrs.	0.12	0.28

From the results in table 7 the mean rates for evolution of water and carbon dioxide would be approx. 0.20 and 0.04 μmoles/hr./g. if the illumination did not affect them. In the case of water the rates are all less than the rates for dark treatment, the latter two being fairly close to it. The carbon dioxide evolution however was in all cases higher than for dark treatment with oxygen and is apparently accelerated by illumination.

Occasionally, illumination of a film yielded much smaller amounts of water and carbon dioxide than in the above examples, which are typical of the large majority of the experiments.

As no water or carbon dioxide appear in the gas phase when the film stands in 50 mm. of oxygen in the dark, it is important to determine whether this is also the case when the film is illuminated.

Acetone Bound Films

The measurements of rates of evolution of water and carbon dioxide from acetone bound films were measured in the same way as these for water bound films. The day to day averages for a film of 0.039 g. zinc oxide hyperfine III are given below. The film was given 4 days preliminary evacuation before rates were measured.

TABLE 8

Film Weight = 0.039

	Average Rate for H_2O μmoles/hr./g.	Average Rate for CO_2 μmoles/hr./g.
12 hours pumping at 10^{-4} 12 hours in contact with cold trap	0.484	0.45
12 hours pumping at 10^{-4} 12 hours in contact with cold trap	1.79	0.23
12 hours pumping at 10^{-4} 12 hours in contact with cold trap	1.48	0.48
12 hours pumping at 10^{-4} 12 hours in contact with cold trap	1.27	0.35

It can be seen that while the rate of water evolution is slowly falling that of carbon dioxide evolution is roughly constant though erratic and is lower/

lower than that for water. As the film is usually illuminated during the period of the latter two days of this treatment, the average of the values obtained during this time is taken, to compare with the rates obtained during illumination in oxygen. These values are

Rate of Water evolution = 1.38 μ moles/hr./g.
Rate of Carbon Dioxide evolution = 0.425 μ moles/hr./g.

The experiment was conducted also with a film of 0.016 g. zinc oxide hyperfine III and the average rates in this period were

Rate of Water evolution = 1.59 μ moles/hr./g.
Rate of Carbon Dioxide evolution = 0.312 μ moles/hr./g.

The similarity between the figures for these two films of different weights is noted. Evidence of an ageing process such as was found with the water bound films was also obtained with acetone bound films. The rates of water and carbon dioxide desorption for acetone bound films were slightly higher than those for water bound films.

Illumination in Oxygen

Acetone Bound Films

Water and carbon dioxide were found in equal quantities after illuminating zinc oxide hyperfine in oxygen. The rates of evolution of water and carbon dioxide,/

dioxide, calculated as amount detected divided by the period of illumination, for several experiments are shown below. The water and carbon dioxide was detected by pumping the gas phase through a liquid oxygen cooled trap immediately illumination ceased. The pressure in the reaction space was reduced to 0.1 mm. or less in 2-3 mins. The contents of the cold trap were then identified by vapour pressure measurements, after separating mixtures by distillation.

TABLE 9

Film Weight g.	Time of Illumination hrs.	Average H_2O rate μ moles/hr./g.	Average CO_2 rate μ moles/hr./g.
0.039	20	0.62	0.62
0.030	21	0.14	0.14
0.091	26	not measured	0.45
0.026	22	0.63	0.63
0.016	18	1.44	1.39

It can be seen from the above that the "photo"-rates of evolution of water and carbon dioxide are very similar in the case of acetone bound films. The rates of carbon dioxide evolution are normally higher than could be expected from dark evolution measurements while the "photo"-rates of water evolution are lower than the "dark"-rates.

A comparison of the amounts of water and carbon dioxide/

dioxide produced with the pressure decrease observed during illumination, however, indicates a direct relationship between these quantities, for example:-

When a reaction flask with a side-arm containing phosphoric oxide or a side-arm immersed in liquid oxygen is used, water or carbon dioxide and water can be con-:tinuously removed from the gas phase. The ΔP against t curves for runs of these types would be expected to have higher rates than these for runs in which no removal of water or carbon dioxide takes place, if the gas phase evolution of these materials is continuous. The following results were obtained during three runs with films of approximately the same weight, being illuminated in 50 mm. oxygen at 25° C. in flasks of types I, II and III.

TABLE 10/

T A B L E 10

Type of Flask	ΔP after 350 min μmoles/g	Ratio of ΔP 350	ΔP after 640 min μmoles/g	Ratio of ΔP 640	ΔP_∞ μmoles/g	Ratio of P_∞	$T_{\frac{1}{2}}$ mins.	Film Weight g.
Type I Flask $H_2O + CO_2$ in situ	20.2	0.87	25.8	0.86	34.8	0.98	252	0.039
Type III Flask H_2O removed	39.2	1.70	50.6	1.68	65.0	1.82	245	0.027
Type II Flask $H_2O + CO_2$ removed	69.4	3.00	90.4	3.00	107	3.00	252	0.030

In the above table the ΔP columns give the pressure decrease observed after 350 and 640 minutes in units of μmoles/g. The ratios referred to are the ratios of the ΔP values in the preceeding column, the value of 3 for the ΔPs observed using type II flask being arbitary. $\Delta P\infty$ is the extrapolated pressure decrease at zero rate while $T_{\frac{1}{2}}$ is the time during which a pressure decrease of 0.5 $\Delta P\infty$ was observed.

It can be seen that the ratios of ΔP values in the three runs after 350 and 640 mins. are approximately equal while the half life times ($T_{\frac{1}{2}}$) of the three runs are similar. Linear, R against log $\Sigma \Delta P$ plots were obtained in all cases and the extrapolated $\Delta P\infty$ values for runs in Type I, Type III and Type II flasks are in the approximate ratio of 1:2:3.

It is noted that in a few experiments, the ratio of ΔP to the amounts of water and carbon dioxide obtained were not in agreement with the above ratios, and that no correction has been made for thermal production of water and carbon dioxide.

It seems clear, on this basis, that water and carbon dioxide are evolved during illumination in quantities which are proportional to the rate of oxygen uptake.

Water/

Water Bound Films

In the case of water bound films, similar evidence that water and carbon dioxide are produced in the gas phase on illumination was obtained. The ratios of the uptake of oxygen to the amounts of carbon dioxide and water produced were different, however, from those found with acetone bound films. Films of low weight 0.02 g. gave only carbon dioxide in measurable quantities and a comparison of two runs with flasks of type I and type II is shown here.

TABLE 11/

T A B L E 11

Type of Flask	Film Weight g.	ΔP after 100 min μmoles/g	Ratio ΔP 100	ΔP after 200 min μmoles/g	Ratio ΔP 200	ΔP after 300 min μmoles/g	Ratio ΔP 300
1) Type I Flask CO_2 in situ	0.017	13.5	1.08	21.2	1.18	25.9	1.13
2) Type II Flask CO_2 removed	0.020	25.0	2.00	36.0	2.00	46.0	2.00

When the gas phase was examined after run 1) in table (11) 5.1 div. of carbon dioxide were found, the total pressure decrease having been 5.2 div. during illumination. This is in agreement with the results in table 11.

When a film of 0.1 g. is illuminated, both water and carbon dioxide are found on examining the gas phase (see table p.68). A comparison of a run in which water was removed during illumination using a type II flask with a phosphoric oxide side-arm, and a run with a type I flask, using 0.1 g. zinc oxide films in both cases, gave the following results.

TABLE /

Run	Film Weight	ΔP after 10 hrs. μ moles	Ratio	ΔP after 15 hrs. μ moles	Ratio	ΔP after 20 hrs. μ moles	Ratio
1) Type I flask	0.10 g.	0.98	1	1.26	1	1.48	1
2) Type II flask, H_2O removed by P_2O_5	0.10 g.	1.84	1.88	2.36	1.87	2.74	1.85

The pressure decrease during Run 1 was compared with the pressure decrease + the water, and the follow-:ing result obtained

Water detected in pumped out gas phase = 1.64 μ moles

Pressure decrease during illumination = 1.48 μ moles.

Pressure decrease: Theoretical pressure decrease had H_2O been removed during illumination

= 1.64 : (1.64 + 1.48) = 1.48 : 3.12 = 1 : 2.1

This is in fairly good agreement with the ratios obtained by comparing the pressure decreases observed in the two runs (table) ompare The ratios obtained with these water bound films are also comparable with the ratios obtained with the acetone bound films (table 10). When a type IV flask is used however the amounts of water and carbon dioxide obtained are less than would be expected from the above results, this probably being due to the more regular film prepared in these flasks and hence more efficient degassing of the oxide.

It seems clear that the carbon dioxide and water are produced in the gas phase as a result of illumina-:tion and that they are produced at a rate proportional to the rate of oxygen uptake. It also appears that the method of determining the amount of these gases present in the gas phase after illumination gives a good approximation to the true value. Losses of water and carbon dioxide will occur during their determination due/

due to adsorption on the glass of the apparatus but these will be small at the low pressures involved.

These results will be considered again in the discussion.

Nitrite

When a film had been illuminated in oxygen, a small amount of nitrite was detected by washing the film with water and testing these washings with Griess-Llosvay reagent (p.41). In a film of 0.1 g. the uptake of oxygen was 5.2 μ moles in 320 hrs. and the nitrite detected was 0.4 μ moles. This is presumably due to the ammonia which is present in the zinc oxide hyperfine as an impurity. The amount is present in all films as an impurity and is small; no correction has been made to the oxygen uptakes measured, as the same proportion of ammonia is present in all films.

The Extrapolated Total Oxygen Uptake

As water and carbon dioxide are being produced in the gas phase during illumination, the observed ΔP value will not correspond directly to the amount of oxygen taken up by the film. While this will not affect the results obtained by the relative rate method, the comparison of extrapolated $\Sigma\Delta P_\infty$ values obtained with/

with different films will only be valid if a correction is made for the amounts of gas phase water and carbon dioxide present. The correction has been made by multiplying $\Sigma\Delta P_\infty$ by the ratio of the pressure decrease observed ($\Sigma\Delta P$) plus the water and carbon dioxide obtained $\Sigma(H_2O + CO_2)$ to the pressure decrease $\Sigma\Delta P$, the new quantity being the oxygen uptake after an infinitely long period of illumination $\Sigma O_{2\infty}$.

$$\Sigma O_{2\infty} = \Sigma\Delta P_\infty \frac{(\Sigma\Delta P + \Sigma(H_2O + CO_2))}{\Sigma\Delta P}$$

The Extent of Oxygen Uptake

From extrapolated $\Sigma O_{2\infty}$ values obtained from the latter linear portions of the R against $\log\Sigma\Delta P$ graphs, some measure of the extent to which a film of zinc oxide hyperfine can take up oxygen, can be obtained. A considerable variation in the $\Sigma O_{2\infty}$ values obtained is evident even in films of the same weight in similar flasks. A number of factors affect the uptake of oxygen and these will now be described. It is noted here that none of these factors affect the general form of the uptake curves.

Pretreatment of Samples

During the preparation of zinc oxide hyperfine, heating in vacuo was applied for different lengths of time/

time in order to remove as much ammonia and carbon dioxide as possible. A number of samples were pre-:pared, containing different amounts of ammonia and, presumably, carbon dioxide. The illumination of these samples, and also analar zinc oxide, gave the following results for ΔP_{∞}. No correction has been made for any water and carbon dioxide appearing in the gas phase during illumination as the quantities were not accurately known but will be similar in each particular case. All samples were illuminated in 50 mm. oxygen at 25° C. with a 250 watt mercury lamp, and $\Sigma\Delta P_{\infty}$ values were extrapolated from R against $\log \Sigma\Delta P$ plots, which were in every case similar to those in figures ( ).

TABLE 12

Sample	Film Weight	ΔP_{∞} μmoles	ΔP_{∞} μmoles/g	NH_3 content μ moles NH_3/g	Time of heating of sample
ZnO A.R. (B.D.H.)	0.093g	0.246	2.844		
ZnO hyperfine I	0.097	0.83	8.55	168 μ moles/g	5 hrs.
ZnO hyperfine IIa	0.104	2.15	20.6	218 μ moles/g	24 hrs.
ZnO hyperfine IIb	0.120	4.58	38.2	41.9 μ moles/g	48 hrs.
ZnO hyperfine III	0.100	5.73	57.3	26.4 μ moles/g	60 hrs.

It can be seen from the above table that as the amount of ammonia present decreases, the amount of oxygen taken/

FIG. 16.

X 8,000

X 40,000

A. B.

ELECTRON MICROGRAPHS.

A) ZINC OXIDE ANALAR. PARTICLE SIZE 2000-3000 Å

B) ZINC OXIDE "HYPERFINE" PARTICLE SIZE 250 Å

C.

c) ZINC OXIDE ANALAR. D) ZINC OXIDE "HYPERFINE"

D.

X-RAY POWDER PHOTOGRAPHS.

taken up, increases, all the $\Sigma \Delta P_{\infty}$ values for "hyper-:fine" films being higher than for the commercial sample.

As treating a zinc oxide film with ammonia, which is dealt with later, increased the uptake of oxygen, it would appear that not all the ammonia is present on the surface, and that it is the reduction of particle size accompanying the removal of ammonia and carbon dioxide which is responsible for the enhanced activity. That some ammonia was present on the surface as shown by the presence of a small amount of nitrite on the surface of illuminated film.

As the effect of the ammonia impurity was small and its further removal from the sample without in-:creasing the temperature, and hence the particle size, being apparently impossible, the most active sample obtained, sample III was used in the experiments described in this work, unless it is otherwise stated.

Crystal Structure

As zinc oxide "hyperfine" was used in this work it was examined by x-ray powder diffraction and compared with photographs obtained for commercial zinc oxide (analar). The photographs for zinc oxide hyperfine III and zinc oxide analar (B.D.H.) are shown in figure (16). It is apparent that the crystal lattice is the same

in/

in both samples, line broadening, however, being observed with the "hyperfine" sample. This was observed by Conn, Humphrey, Magee and Wallace[22], who explain the broadening in terms of a high degree of lattice disorder coupled with small particle size.

The Effect of the Binding Liquid on the Oxygen Uptake

In order to form a film of zinc oxide in a reaction vessel, the oxide had to be made into suspension with a liquid which was later removed by evaporation. Acetone and water were the liquids used in this work for ease of removal in the case of acetone and in the case of water because it was an impurity already present and thus unlikely to affect the activity of the film.

The possibility of chemisorption of acetone with subsequent photo-oxidation was realised and a comparison of $\Delta O_{2\infty}$ values obtained with the two binding liquids under otherwise identical condition is given below. The temperature was 25° C. and the initial oxygen pressure was 50 mm. in every case, and a correction has been made for the water and carbon dioxide detected in the gas phase.

TABLE 13/

TABLE 13

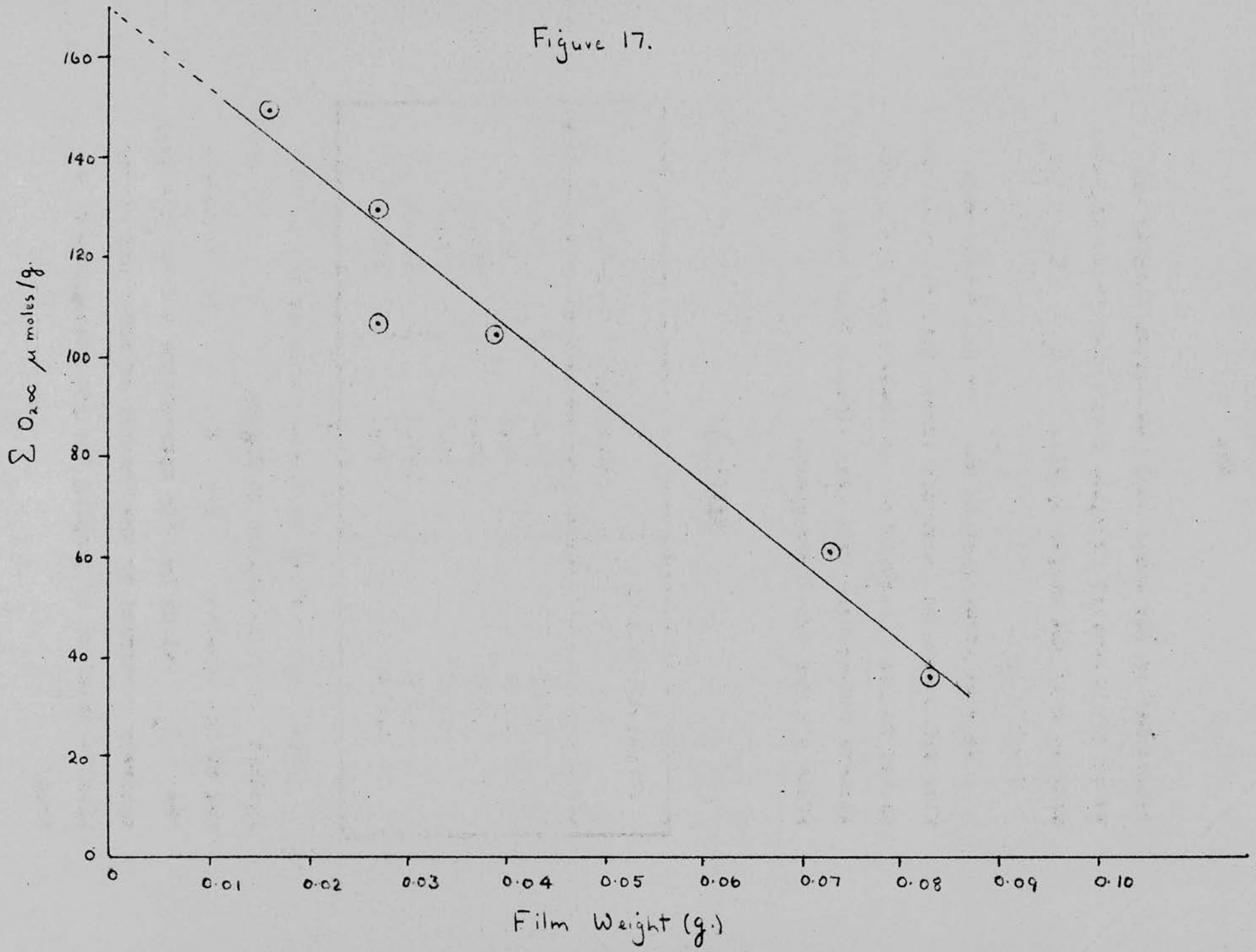
Sample	Wt. of film	Type of flask	Acetone Bound $\Delta O_{2\infty}$ μmoles/g	Water Bound $\Delta O_{2\infty}$ μmoles/g
Zinc Oxide hyper-:fine IIa	0.120g	I	38.2	41.0
ZnO hyperfine III	0.100g	IV	191	150
ZnO hyperfine III	0.020g	IV	615	630

It can be seen that only in one case was any appreciable difference, between the uptake of films bound with the two liquids, found. It must be con-:cluded therefore that no real difference between films bound with acetone and water exists and that in the case of zinc oxide there is no photo-oxidation of residual acetone.

The Effect of Film Weight

As can be seen from the previous results, films of low weight (0.02 g.) give a very much higher value of $\Sigma O_{2\infty}$ in μmoles/g. than do films of 0.1 g. zinc oxide. The extrapolated $\Sigma \Delta P_{\infty}$ values for a number of acetone bound films of different weights which were illuminated in 50 mm. of oxygen at 25° C. in spherical type reaction flasks are set out below. $\Sigma \Delta O_{2\infty}$ values have been calculated/

Figure 17.


160
140
120
100
80
60
40
20
0
$\Sigma O_{2\infty}$ μ moles/g.
0
0·01
0·02
0·03
0·04
0·05
0·06
0·07
0·08
0·09
0·10
Film Weight (g.)

calculated on the basis that the carbon dioxide and water are liberated in equal quantities which together make up $\frac{2}{3}$ of the oxygen uptake. $\Sigma O_2 = \Sigma H_{20} + \Sigma CO_2 + \Sigma \Delta P = 3\Sigma \Delta P$.

In some cases type II and type III flasks were used and water, or water and carbon dioxide, were re-:moved during illumination: in these cases the appro-:priate corrections have been made. Zinc oxide hyper-:fine III was used throughout.

TABLE 14

Weight of film (g)	$\Sigma \Delta P_\infty$ μ moles/g.	$\Sigma O_{2\infty}$ μ moles/g.
0.083	17.8	35.6
0.073	60.1	60.1
0.039	34.8	104.4
0.027	65.0	130.0
0.027	107.0	107.0
0.016	49.9	148.7

The $\Sigma O_{2\infty}$ values in the above table are plotted against the film weights in figure (17). While the use of the equality $\Sigma \Delta P = \Sigma H_2O = \Sigma CO_2$ to obtain the $\Sigma O_{2\infty}$ values is only approximate and has not been entirely justified by the amounts of water and carbon dioxide obtained by pumping the gas phase through a cold/

cold trap in every case, it can be seen that an approxi-:mately straight line relationship between the weight of a film and its ability to adsorb oxygen exists.

This is probably due to the powder particles being superimposed in the heavier films and obstructing the diffusion of oxygen and the passage of light. The linear relationship suggests that the optimum value of $\Sigma O_{2\infty}$, when no such obstruction exists will lie in the region where the line intersects the $\Sigma O_{2\infty}$ axis, i.e. 170 μ moles/g. for this type of flask, and this method of preparing films.

The Effect of Using Type IV Flasks

When a film is prepared in a type IV flask by allowing a suspension of zinc oxide hyperfine to settle out, an even layer of oxide, of predetermined diameter, results. The maximum surface of oxide is thus exposed to the oxygen, and less obstruction of light is caused then by the other method of preparing films. It is thus to be expected that these films will have a larger uptake of oxygen than others, and this has been bourne out by experiment. A comparison of uptakes by films in spherical and type IV flasks is given below, zinc oxide hyperfine III having been illuminated in 50 mm. oxygen at 25° C. in all cases, and correction for the amounts of water and carbon dioxide detected in the pumped/

pumped out gas phase having been made.

TABLE 15

Weight of Film	Type of Flask	$\Sigma O_{2\infty}$ μmoles/g	Binding Liquid
0.02 g.	I	179	H_2O
0.02 g.	IV	630	H_2O
0.10 g.	I	171	H_2O
0.10 g.	IV	241	H_2O

It can be seen that a much larger difference between the results obtained with the two types of flask exists with films of low weight (0.02 g.) than exists with film of 0.1 g. zinc oxide. Similar results have been obtained using acetone bound films.

It can be seen from the above, that any attempt to arrive at the number of sites available on the zinc oxide for the adsorption of oxygen will be governed by the type of film prepared, and it would appear that not all the sites present in the zinc oxide are taking part in the photo-uptake.

By taking a particular type of flask, however, and using the same film weight in every case a measure of the number of sites on this surface can be estimated approximately./

approximately. A 0.1 g. film, water bound, in a type IV flask has been used as the standard surface and results obtained with this type of film in gases other than oxygen, are compared with the oxygen value.

The $\Sigma(O_2)_\infty$ value is obtained from the R against log ($\Sigma\Delta P$) plots for films of this type of which run (1) is an example. In this case a break occurs after approximately 6.25 μ moles pressure decrease and a final extrapolated pressure decrease of 19.6 μ moles is obtained by extrapolating the portion of the rate curve after the break. In many cases a film could not be illuminated for a sufficient length of time to enable sufficient oxygen to be taken up and the extrapolated $\Sigma\Delta P_\infty$ values from these films agrees closely with that obtained from the initial portion of the run (1) rate curve. (R against log ($\Sigma\Delta P$) A number of these extrapolated values, corresponding to the initial linear portion of the R against log$\Sigma\Delta P$ line in run 1. A number of these values are shown below.

TABLE 16

Total Pressure Decrease Observed ($\Sigma\Delta P$) μ moles	$\Sigma\Delta P_\infty$ μ moles
3.04	9.4
7.16	11.5
6.50	11.1
2.48	11.4
Run 1 1st linear portion	11.3

No/

No correction has been made here for the evolution of water and carbon dioxide as very similar quantities were obtained in each case

In most of these runs a non-linear R against log $\Sigma\Delta P$ line was observed until an uptake of approximately 2 μ moles had taken place.

It is thus considered that while a value of $\Sigma\Delta P_{\infty}$ in the region of 11 μ moles is fairly reproducible for films of this type, the larger value obtained in run 3 ($\Sigma\Delta P_{\infty}$ = 19.6 μ moles) is a more accurate measure of the total pressure decrease which can take place. The films capacity for oxygen photo-sorption $\Sigma O_{2\infty}$ is 24.1 μ moles in this case, or 241 μ moles/g.

Surface Area of Zinc Oxide Hyperfine Film

If zinc oxide hyperfine is assumed to consist of spherical particles having the same density as zinc oxide the surface area of the sample can be calculated from a knowledge of the diameter of the particles.

The mean diameter of the particles in zinc oxide hyperfine sample III was found to be in the region of 250 $\mathring{A}$ from electron-micrographs figure 16 and the sur-:face area to be of the order of 4.4×10^5 cm^2/g.

Calculation/

Calculation

Surface area per g. of powder (S) = ns

where n = number of particles/g.

s = surface area of 1 particle

ρ = density of ZnO

D = mean particle diameter.

$$n = \frac{\text{wt. of Powder}}{\text{wt. of 1 particle}} = \frac{1}{\rho \frac{4}{3}\pi(\frac{D}{2})^3}$$

$$s = 4\pi(\frac{D}{2})^2$$

$$\therefore \quad S = ns = \frac{6}{\rho D} \quad \text{and} \quad \rho = 5.47 \text{ g./ml.}, \quad D = 250 \times 10^{-8} \text{ cm.}$$

By substitution $S = \frac{6 \times 10^8}{5.47 \times 250}$

$= 4.39 \times 10^5 \text{ cm}^2/\text{g.}$

An uptake of 241 μ moles of oxygen per g. is equivalent to $241 \times 6.02 \times 10^{23} \times 10^{-6}$ molecules of oxygen where 6.02×10^{23} is taken as Avogadro's Number.

This is equal to 1.450×10^{20} molecules of oxygen /g. As the surface area of 1g. of this sample is approximately 4.4×10^5 cm^2 this would represent a surface coverage of

$1.45 \times 10^{20}/4.4 \times 10^5$ molecules per cm^2

$= 3.3 \times 10^{14}$ molecules/cm^2.

As not all the surface is available for uptake due to aggregation of particles and the thickness of the/

the film the actual coverage will be higher than this. The percentage coverage of the surface can be calculated, however, on the basis that the entire surface is available.

Taking the diameter of an oxygen molecule as approximately 3 $\mathring{A}$, from gas viscosity, the area occupied becomes $\frac{\pi}{4} 9$ $\mathring{A}^2$ per molecule.

The total number of molecules on 1g. of oxide
$= 1.45 \times 10^{20}$ and thus the area covered
$= 1.45 \times 10^{20} \times \frac{\pi}{4} \times 9 \times 10^{-16}$ cm^2
$= 1.02 \times 10^5$ cm^2

The surface area of 1g. of oxide $= 4.5 \times 10^5$ cm^2 and the apparent coverage becomes $\frac{1.02}{4.5} \times 100$ %

$= \underline{22.8\%}$

<u>The Effect of Change in Pressure on the Rate of Oxygen Uptake</u>

The relative rate method (p.38) was used to determine the effect of change in pressure on the oxygen uptake; rates at different oxygen pressures being compared with the rate at 50 mm. oxygen to give a relative rate. Illumination was kept constant and the temperature was maintained at 25° C. throughout the experiments. Two methods, one for pressures above 0.5 mm. and one for pressures below this, were used to obtain relative rates/

rates and these methods are now described.

Pressures above 0.5 mm.

Relative rates were obtained during three runs (runs 6, 7 and 8) using zinc oxide hyperfine sample III in runs 6 and 7 and sample I in run 8. Run (6) is now described in detail.

0.070 g. of zinc oxide, water bound in a type IV flask was illuminated in 1.23 mm. of oxygen until a 4 div. decrease in pressure had taken place. Rate values were calculated over the last two divisions only as irregularities in the early stages of illumination are often observed, probably due to heating of the film. The pressure was now rapidly reduced to 0.70 mm. and rates were calculated over 1 div. after the system had been allowed to reach equilibrium for 1 div. The pressure was now raised to 10 mm. and rates taken during an uptake of 4.5 divisions when the pressure was finally raised to 50 mm. and rates were again calculated. Gas pressures were measured using the Bourdon gauge or the manometer, the gauge sensitivity being 0.0552 mm/div. The rate values obtained were plotted against log ΔP and relative rates obtained by comparing a point on the line drawn through each set of rate values to the intercept of the R against log $\Sigma \Delta P$ line at 50 mm. with the log $\Sigma \Delta P$ axis, with the point on the/

the 50 mm. line at the same log$\Sigma\Delta$P value.

The rate values obtained are given in table 17, and the R against log $\Sigma\Delta$P graphs are shown in figure 18(a). The initial pressures are taken as the pressure at which the relative rates are measured as little change in pressure occurs during illumination. Re-:lative rates derived from this run and runs 7 and 8 are given in table 18.

TABLE 17/

Fig. 18 a.

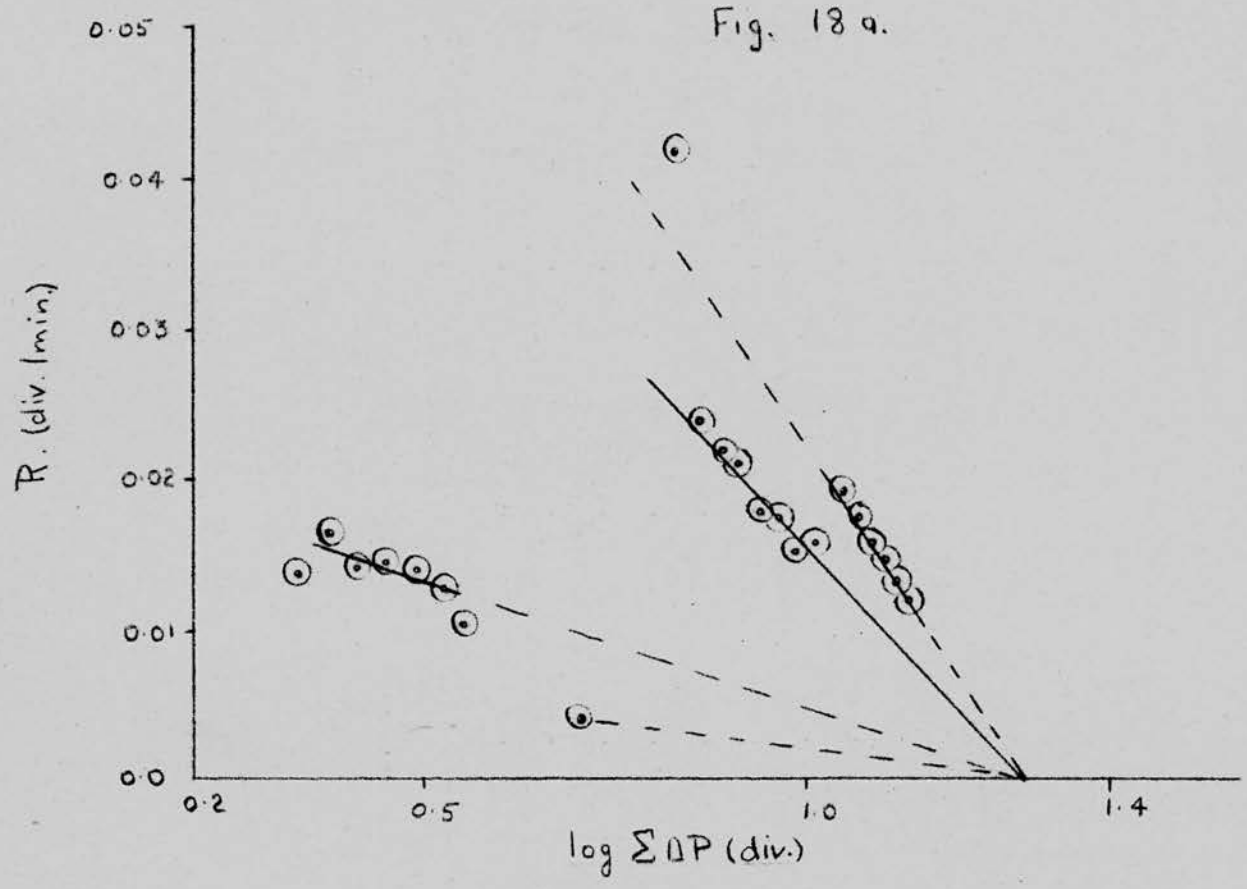


Fig. 18 b.

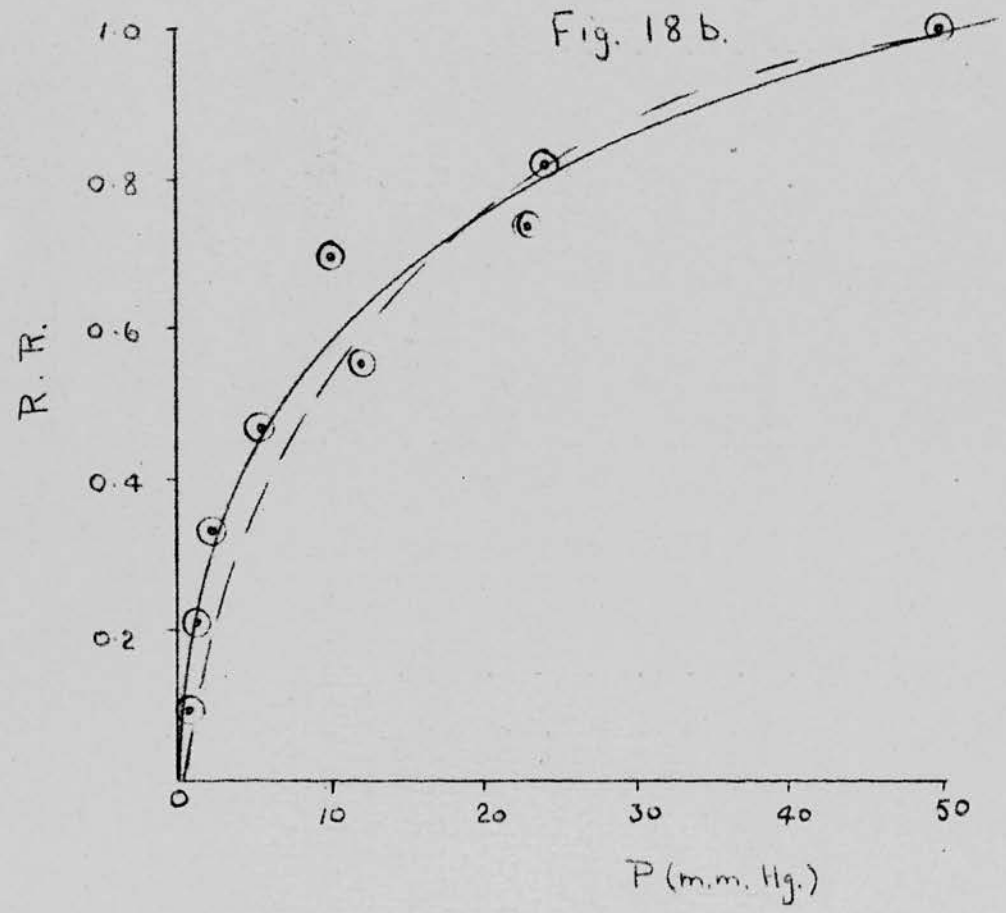


TABLE 17 RUN 6

Initial Pressure 1.12mm		Initial Pressure 0.70mm		Initial Pressure 10mm		Initial Pressure 50mm	
R div/min	log ($\Sigma\Delta$P div)	R div/min	log ($\Sigma\Delta$P div)	R div/min	log ($\Sigma\Delta$P div)	R div/min	log($\Sigma\Delta$P div)
0.0136	0.327	0.0041	0.710	0.0416	0.830	0.0190	1.051
0.0163	0.376			0.0238	0.860	0.0174	1.071
0.0140	0.419			0.0218	0.889	0.0158	1.088
0.0143	0.458			0.0208	0.916	0.0145	1.106
0.0139	0.495			0.0178	0.942	0.0132	1.122
0.0125	0.528			0.0172	0.966	0.0120	1.139
0.0100	0.560			0.0151	0.989		
				0.0156	1.011		

TABLE 18

R.R.	P m.m.(Hg)
1.0	50
0.82	24
0.74	23
0.53	12
0.70	10
0.47	5.5
0.34	2.0
0.21	1.1
0.09	0.7

When the R.R. values are plotted against P a curve is obtained which approximates to a Langmuir isotherm for dissociation type adsorption, the equation being of the type $AR.R. = \frac{B\sqrt{P}}{B\sqrt{P} + 1}$.

It was found that the experimental points lie close to a theoretical line drawn from values obtained from the equation

$$0.4\ (R.R.) = \frac{0.097\sqrt{P}}{0.097\sqrt{P} + 1}$$

which is shown by a continuous line in figure 18b. A similar theoretical line of the non-dissociation type could also be drawn through the experimental points and the/

the best curves of this type, represented the equation.

$$0.8\ (R.R.) = \frac{0.08\ P}{0.08\ P + 1}$$

is shown as a dotted line in figure 18b.

From figure 18b it is not possible to decide whether the experimental results can be represented by one or other of these curves, although the curve from the equation for dissociation type adsorption would appear to give the better approximation. Experiments at lower pressures were therefore carried out.

Pressures below 0.5 mm.

8 divs. (0.442 mm.) of oxygen was admitted to a film of 0.060 g. zinc oxide hyperfine III water bound in a type IV flask, which was illuminated until the pressure remained constant for several hours. During the illumination a pressure decrease of 6 divs. took place and it was found that the residual gas was not condensable. As no pressure rise takes place, when a film which has taken up oxygen, is illuminated in vacuo, it was concluded that this gas had been evolved during illumination. As the pressure had remained constant after a pressure decrease of 6 div. had taken place it was assumed that the rate of evolution was proportional to the rate of oxygen uptake and the ΔP values obtained were increased by a factor of 8/6.

50 mm/

50 mm. of oxygen were now admitted to the reaction space and illuminated until a pressure decrease of 5 div. had taken place. As a slow evolution of a non-condensable gas is observed only when a water bound film which has not taken up oxygen is illuminated in vacuo (p.59) no correction was made to the $\triangle P$ values obtained on this basis. A very small amount of con-:densable gases were found in the gas phase by the usual pumping procedure but as this was less than 1 div. it could not be measured accurately and no correction has been made. The rate values were calculated from the uptake isotherm; rate values obtained during the illuminations in 8 div. and 50 mm. of oxygen are given in table 19, below, and the plot of R against log $\Sigma\triangle P$ is shown in figure 19a.

TABLE 19/

Fig. 19 a.

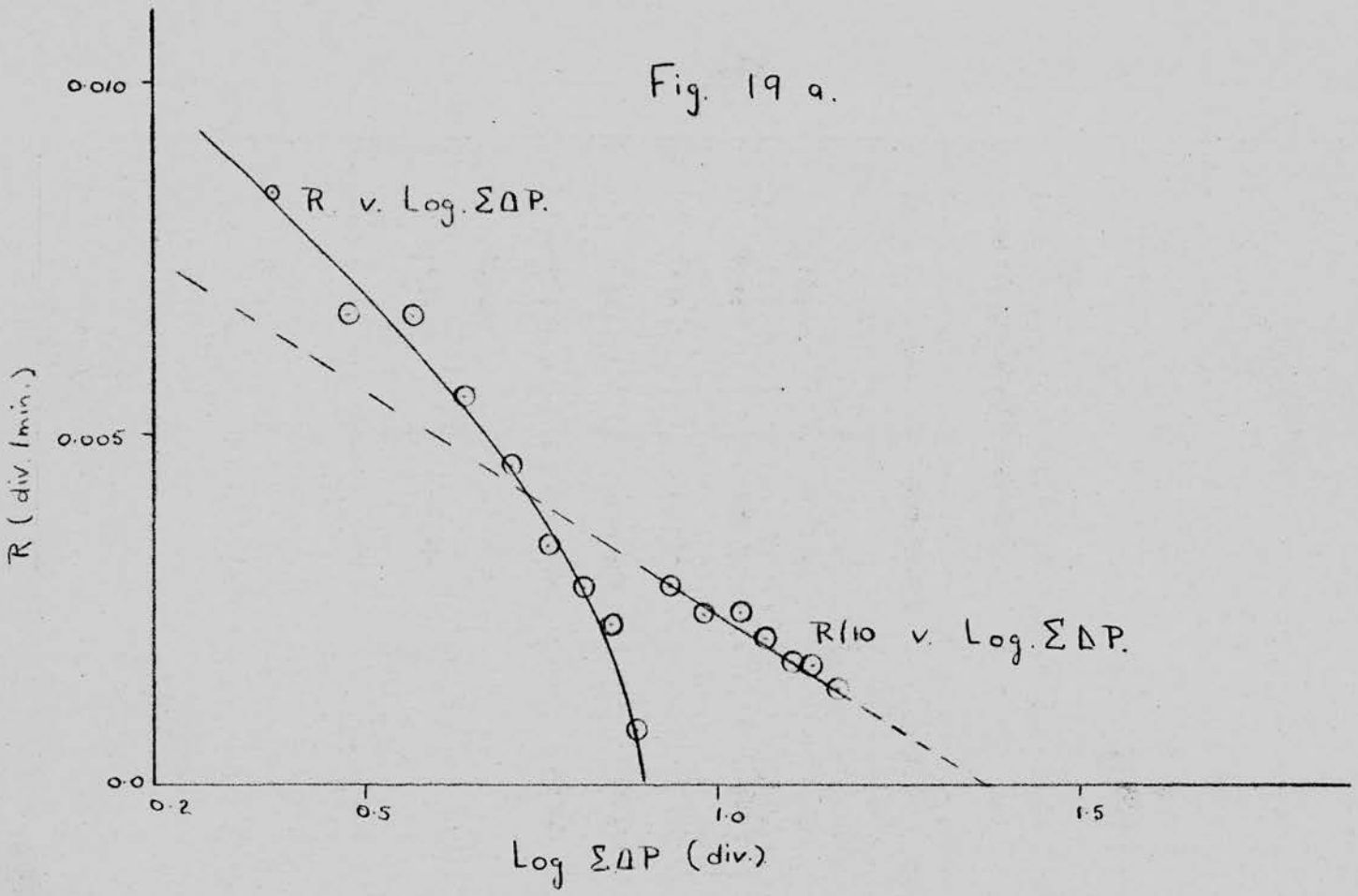


Fig. 19 b.

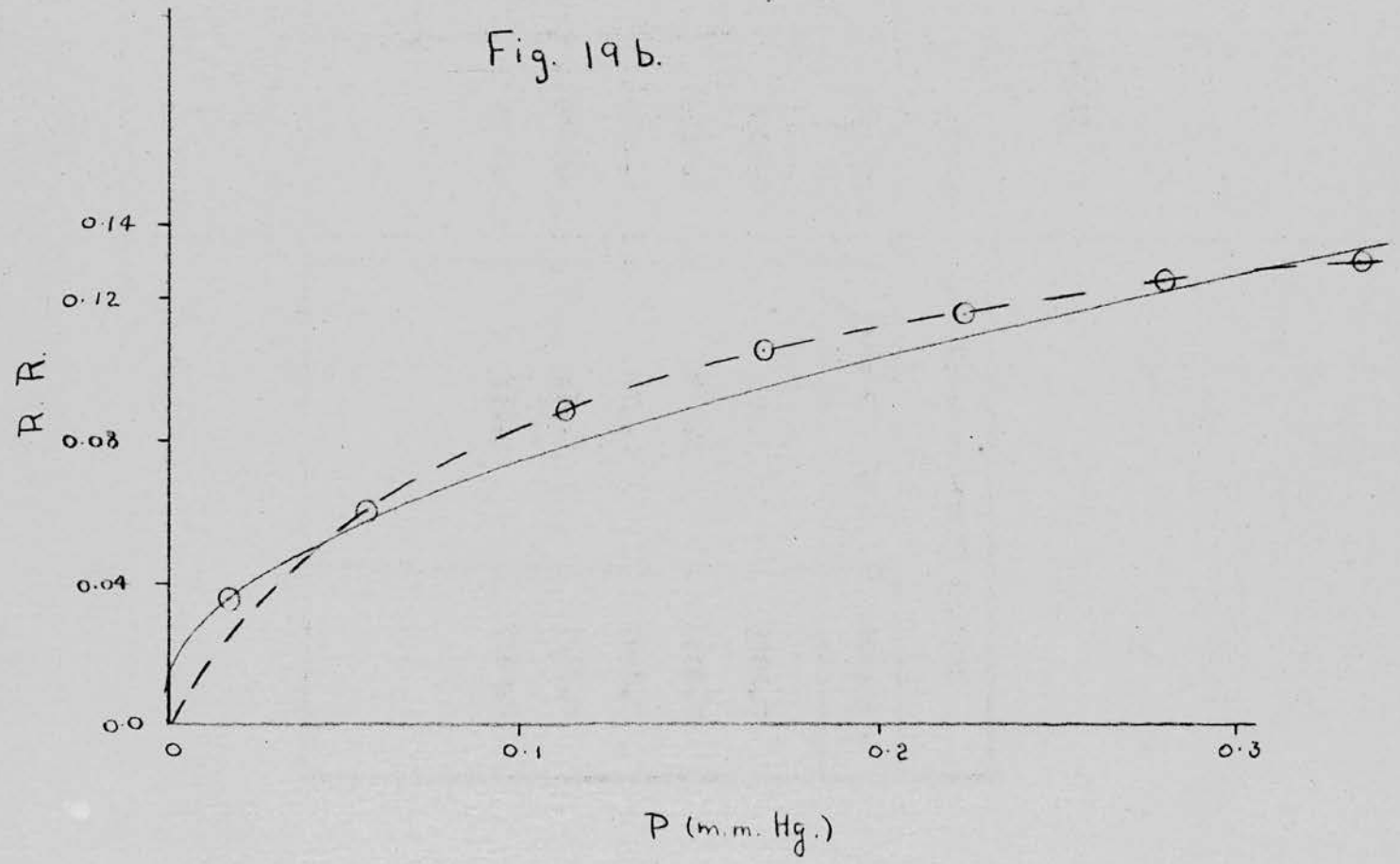


TABLE 19 RUN 9

Initial Pressure 0.442 mm. (8 div.)				Initial Pressure 50 mm	
R div/min	log ($\Sigma\Delta$P div)	R div/min	log ($\Sigma\Delta$P div)	R div/min	log ($\Sigma\Delta$P div)
0.0095	0.202	0.0045	0.699	0.0295	0.929
0.0084	0.368	0.0034	0.753	0.0250	0.978
0.0067	0.476	0.0028	0.802	0.0250	1.021
0.0067	0.564	0.0023	0.844	0.0216	1.061
0.0055	0.637	0.0008	0.884	0.0183	1.096
				0.0176	1.130
				0.0144	1.161

In figure (19b) a smooth surve has been drawn through the results obtained during very low pressure part of the run. The R against log $\Sigma\Delta$P graph for the 50 mm. pressure part can be seen to be linear and a straight line is drawn through the points and extended back to enable rates to be interpolated at ΔP values between 0 and 8. Relative rates were calculated by dividing the rates at various low pressures by the interpolated rates at the same pressures from the 50 mm. line. The relative rates calculated are given in table 20, none having been taken from the initial part of the rate curve as irregularities in rate curves during the initial stages of illuminations have been noted in some films.

TABLE 20

R.R.	P m.m.
0.127	0.331
0.123	0.276
0.114	0.221
0.104	0.165
0.087	0.110
0.059	0.055
0.034	0.017

The relative rates in the above table are plotted against pressure in figure 19b. The theoretical isotherm/

isotherm obtained from the equation

$$0.4\ \text{R.R.} = \frac{0.097\ \sqrt{P}}{0.097\ \sqrt{P} + 1}, \quad \text{(p.96)}$$

is shown as a continuous line, as in figure 18b. The broken line represents the equation,

$$6.1\ (\text{R.R.}) = \frac{10.1\ P}{10.1\ P + 1},$$

which can be seen to pass through all the experimental points except one, and would thus appear to be the more representative of the two isotherms. This equation, however, would mean that R.R. would have a value of 0.142 at $P \simeq 0.6$ and a maximum value of 0.164. If this were the case, a transition between this type of adsorption and, either, dissociative type adsorption, or non-dissociative type adsorption, as represented by the curves in figure (18b) must take place in the region between 0.33 and 1 mm. The other alternative is that the dissociative type of adsorption takes place at all pressures up to 50 mm. and can be represented by the equation given. As no evidence of any transition from one type of adsorption to the other has been obtained and good agreement with the dissociative type adsorption equation was found over the whole range of relative rate measurements, it is considered that the latter alternative best describes the results of these experiments, and that the adsorption of oxygen is of the/

the dissociative type.

Temperature Coefficient

The temperature coefficient of the photo-sorption of oxygen was investigated using the relative rate method by plotting rates of reaction against $\log \Sigma \Delta P$.

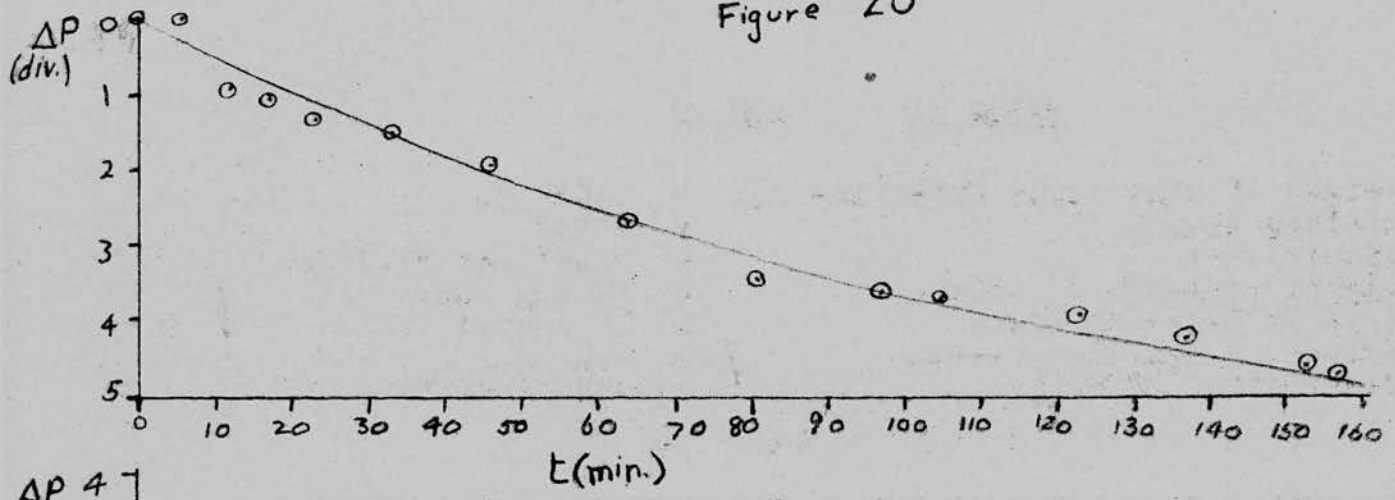
After the usual evacuation, 50 mm. of oxygen was admitted to the reaction volume and the film was illuminated at 25° C. The reaction was followed until the rate curve had been established when the temperature of the thermostat was quickly raised to about 40° C. and the new rate curve was established. The tempera-:ture was now returned to 25° C. and the rate curve established once again. Plotting rates against log ($\Sigma \Delta P$) gave a straight line for each temperature, the lines intersected on the log ($\Sigma \Delta P$) axis.

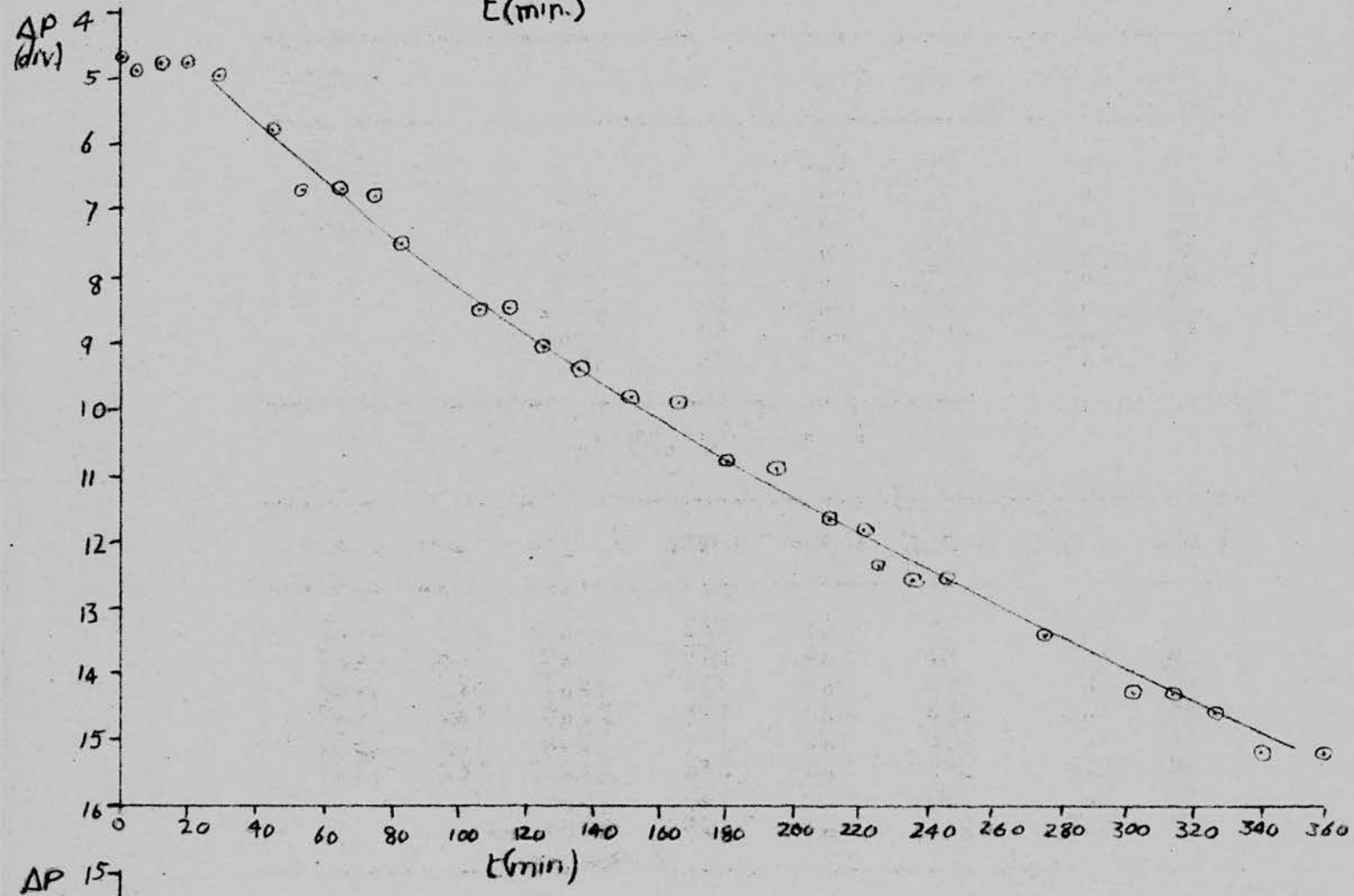
The changes in temperature were made as rapidly as possible and the system was given some time to regain equilibrium before rate values were again taken.

The results of two experiments carried out in this way with film of 0.02 g. and 0.1 g. ZnO hyperfine III are given in tables (21 and 22) and figures (20 and 21).

TABLE 21/

Figure 20


ΔP
(div.)
0
1
2
3
4
5
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160
t(min.)


ΔP
(div.)
4
5
6
7
8
9
10
11
12
13
14
15
16
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360
t(min)

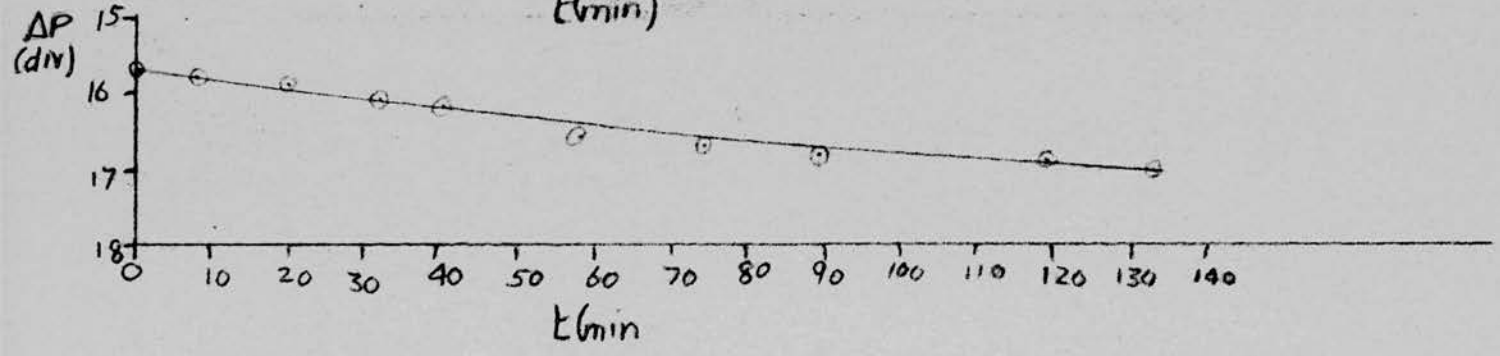

ΔP
(div)
15
16
17
18
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140
t(min

TABLE 21 RUN 10

Weight of Zinc Oxide Hyperfine III = 0.022 g.
Binding Liquid = Water
Temperature = 24.9° and 37.7°C.
Oxygen Pressure (Initial) = 50 mm. (Hg)
Type of Reaction Vessel = IV silica
Volume of Reaction Vessel = 60.4 ml.
Sensitivity of Gauge = 0.0552 mm/div.

T = 24.9° C.

t min	ΔP div	t min	ΔP div	t min	ΔP div	t min	ΔP div
0	0.0	81	3.4			88	16.8
6	0.0	97	3.6	0	15.7	119	16.9
12	0.9	105	3.7	8	15.8	133	17.0
17	1.1	123	3.9	20	15.9		
23	1.3	137	4.2	32	16.1		
33	1.5	153	4.6	40	16.2		
46	1.9	156	4.7	58	16.6		
64	2.7			74	16.7		

T = 37.7° C.

t min	ΔP div	t min	ΔP div	t min	ΔP div	t min	ΔP div
0	4.7	76	6.8	181	10.8	302	14.3
5	4.9	84	7.5	196	10.9	314	14.3
12	4.8	107	8.5	211	11.7	326	14.6
20	4.8	116	8.5	221	11.8	340	15.2
29	5.0	126	9.1	226	12.4	360	15.4
45	5.8	137	9.4	236	12.6	382	15.7
54	6.7	152	9.7	246	12.6		
63	6.7	166	9.9	275	13.4		

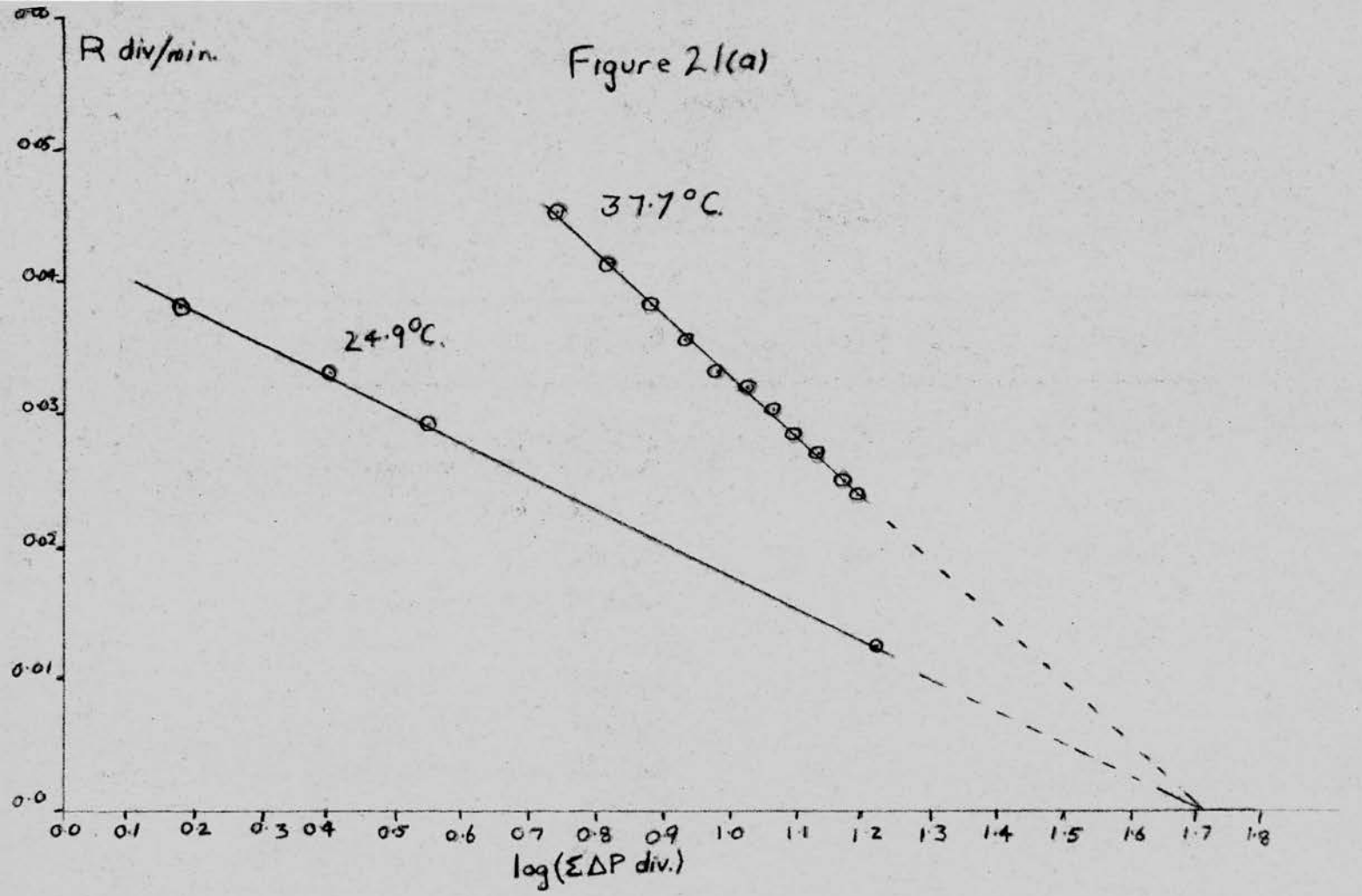


Figure 21(a)

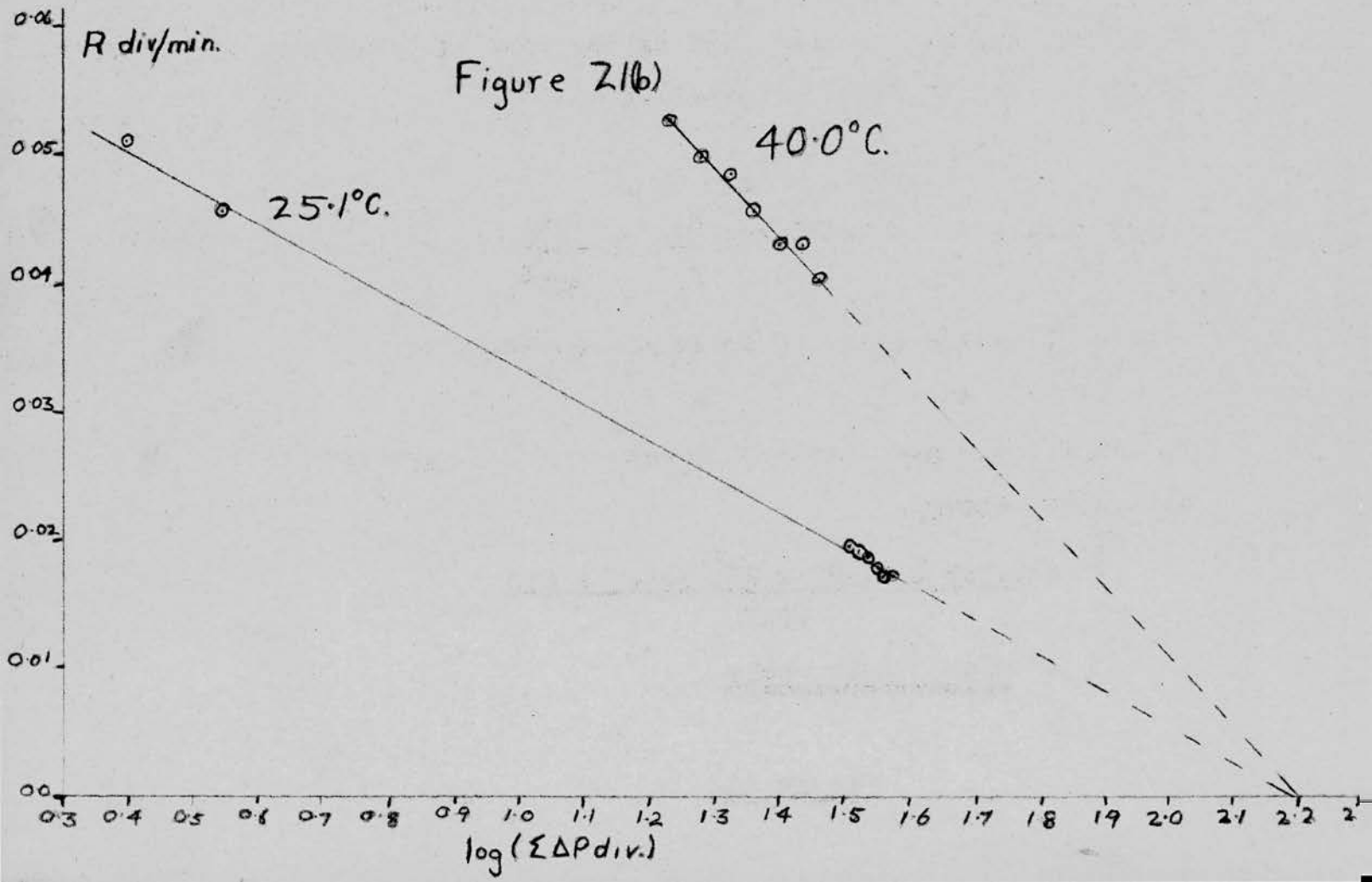


Figure 21(b)

TABLE 21 (cont.)

R div/min	log$\Sigma\Delta$P div	R div/min	log$\Sigma\Delta$P div
0.0500	-0.301	0.0455	0.740
0.0385	0.176	0.0417	0.813
0.0334	0.398	0.0384	0.875
0.0294	0.544	0.0358	0.929
		0.0334	0.978
0.0125	1.218	0.0322	1.021
		0.0303	1.061
		0.0286	1.097
		0.0270	1.130
		0.0250	1.162
		0.0238	1.190

From figure 21a the ratio of the rate of reaction at 25° C. and 37.7° C. is obtained as:-

$$R_{37.7^\circ C.} / R_{25^\circ C.} = 1.85$$

Using formula $E = 2.303 \log \frac{R_2}{R_1} . R. \frac{T_1 T_2}{T_2 - T_1}$

where $\frac{R_2}{R_1}$ is the ratio of Rates at temperatures T_2 and T_1, R = gas constant in cals. E = apparent activation energy.

$$E = \frac{2.303 \times 0.267 \times 2 \times 310.7 \times 298}{12.7}$$

$$= \underline{8.97 \text{ kcals./mole}}$$

TABLE 22/

TABLE 22 RUN 11

Weight of Zinc Oxide Hyperfine III = 0.101 g.
Binding Liquid = Water
Temperatures = 25.1° C. and 40.0°C.
Oxygen Pressure (Initial) = 50 mm (Hg)
Type of Reaction Vessel = IV silica
Volume of Reaction Vessel = 60.9 ml.
Sensitivity of Gauge = 0.0552 mm/div.

R div/min 25.1°C	log$\Sigma\Delta$P div	R div/min 40.0°C	log$\Sigma\Delta$P div
0.0565	0.176	0.0529	1.230
0.0510	0.398	0.0500	1.279
0.0455	0.544	0.0482	1.322
		0.0455	1.362
0.0195	1.512	0.0430	1.398
0.0190	1.525	0.0430	1.432
0.0185	1.538	0.0400	1.462
0.0177	1.550		
0.0133	1.562		
0.0133	1.574		

These results are expressed graphically in figure 21b

From figure 21b

$$\log (R_{40.0°C.}/R_{25.1°C.}) = 0.292$$

$$\therefore \quad E = 2.303 \times 0.292 \times 2 \times \frac{313 \times 298.1}{14.9}$$

$$= \underline{8.50 \text{ k cals/mole}}.$$

It would thus appear that the apparent activation energy for the photo-sorption of zinc oxide between 25° C. and 40° C. is in the region of 8.5 k cals/mole, for the experimental conditions, measured at the second linear portion of the R against log $\Sigma\Delta$P curve.

Illumination/

Illumination with λ = 3650 A light

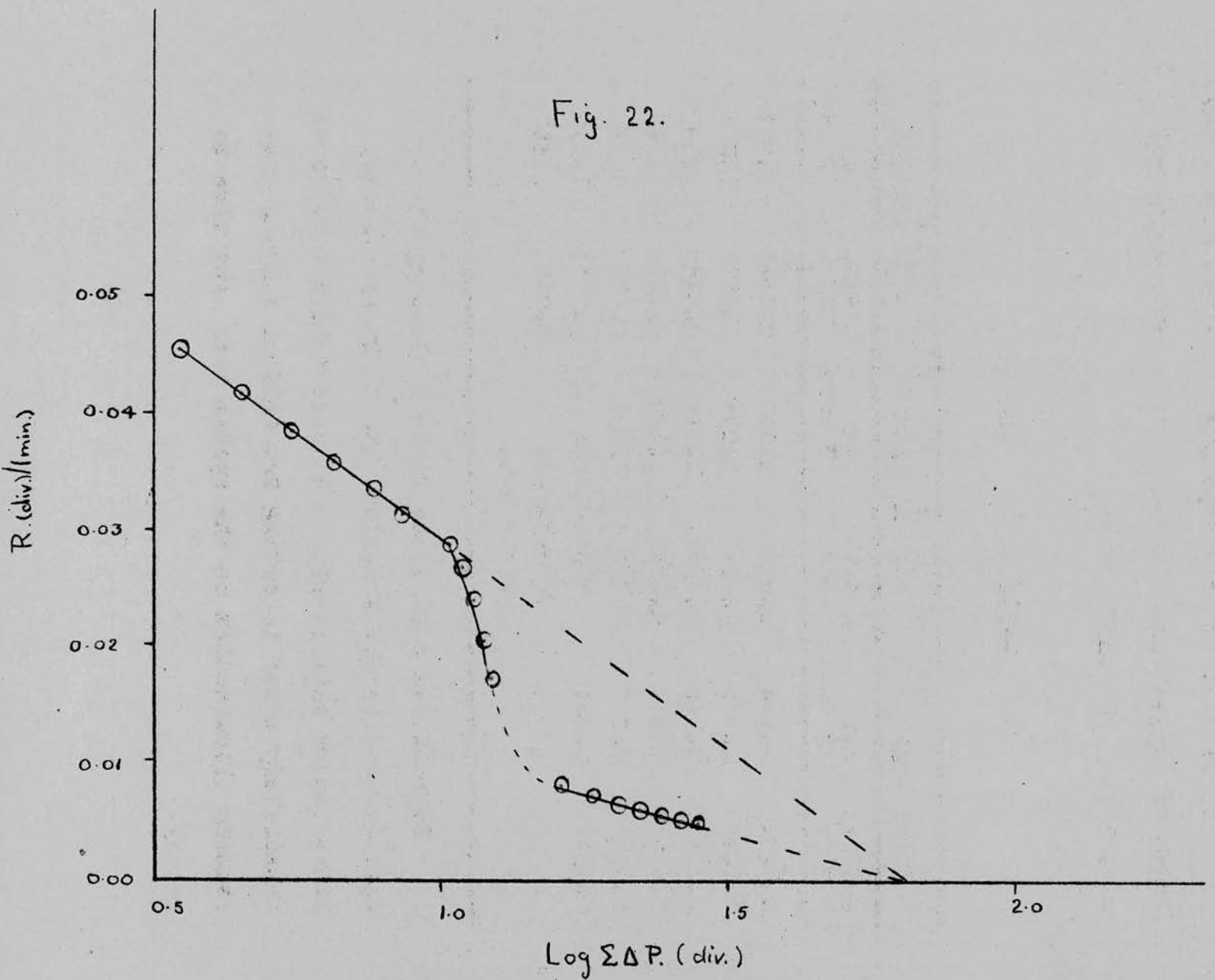
The fundamental absorption band of zinc oxide lies below 4000 A; the main line in the spectrum of the mercury lamp, in this region, being λ = 3650 Å. It is of interest, therefore, to examine the effect of illuminating a film of zinc oxide, with light of this wavelength only, on the rate of oxygen uptake.

A fresh film of 0.1 g. zinc oxide hyperfine in a type IV flask was illuminated in white light, after the usual evacuation until an R against log $\Sigma\Delta$ P rate curve had been established, (after 10 divs.) A 2 mm. Wood's glass filter was now placed in the light path, allowing only light of 3650 Å to reach the zinc oxide. The reaction rate dropped gradually. Illumination was interrupted here for 12 hours. On resuming illumination with λ = 3650 Å light a linear R against log ($\Sigma\Delta$ P) plot was obtained over 18 divisions pressure drop.

The transmission of the Wood's glass filter was determined with respect to 3650 A light and the intensity of illumination with and without the filter was measured using a "barrier" type photocell and suitable neutral filters so that the photo-current measured was similar in both cases.

It/

Fig. 22.



It was assumed that the photo-current produced was independent of wavelength over the range of wave-:lengths concerned.

The results of this experiment are now given, the rates of oxygen uptake in table (23) being expressed graphically in figure (22).

TABLE 23 RUN 12

White light		3650 Å light		3650 Å light	
R div. min.	log (ΣΔP div)	R div. min.	log (ΣΔP div)	R div. min.	log (ΣΔP div)
0.0454	0.544	0.0287	1.012	0.0083	1.204
0.0416	0.653	0.0269	1.032	0.0072	1.255
0.0384	0.740	0.0238	1.052	0.0065	1.301
0.0357	0.812	0.0208	1.070	0.0061	1.342
0.0333	0.875	0.0172	1.088	0.0054	1.380
0.0312	0.929	Illumination interrupted for 12 hrs.		0.0053	1.415
				0.0051	1.447

Rate values during the first 3 divs. uptake have been omitted as the R against log ΣΔ P curve became linear after this period. No rate values were taken immediately after inserting the optical filter, or re-:suming illumination, as the system took some time to reach/

reach equilibrium. From figure(22), it can be seen that a rate of uptake with 3650 Å light relative to the rate with white light can be obtained by comparing values on the intersecting lines.

The relative rate obtained from figure(22) is 0.36 for 3650 Å light with respect to white light

Transmission by 3650 Å filter = 62.9% 3650 Å light

Assuming that the rate of oxygen uptake is pro-:portional to light intensity, the relative rate would be $0,36 \times \frac{100}{62.9}$ for 3650 Å if the filter had 100% light transmission i.e. R.R. = 0.57.

It would thus appear that 57% of the oxygen uptake observed is due to light of 3650 Å wavelength. The percentage of light of this wavelength in the total "white light" illumination was found to be 0.22% by the photo-cell method described above. After correction has been made for the absorption of the filter this becomes 0.35%.

It would thus appear that light of λ = 3650 Å is of primary importance in the photo-sorption of oxygen by zinc oxide.

The/

The slow fall in rate when the optical filter was placed in the light path is in accordance with a gradual decay of sites no longer being activated, the linear R against log ($\Sigma\Delta$ P) plot, obtained for the 3650 Å light after the film had stood in the dark, being expected on this basis.

Light Intensity and Oxygen Uptake

It was assumed in the last section that the rate of oxygen uptake was proportional to the incident light intensity; the following experiment demonstrates the validity of this assumption. The relative rate method was used, the intensity of illumination being varied by inserting neutral filters into the light path, which was of white light from the mercury lamp, as the use of monochromatic light would involve the measurement of extremely small rates.

A film of 0.1 g. zinc oxide hyperfine III was illuminated in a type IV flask at 25° C, until the second linear portion of the R against log ($\Sigma\Delta$ P) graph was reached (after 12 divs.). A neutral filter of 47% transmission was now placed in the light path and the rate of oxygen uptake measured during a pressure decrease of 8 div.

This/

This filter was then replaced by one giving 88% transmission and the rate of uptake was measured during a further 6 divisions, when this filter was removed and illumination at the original intensity was resumed during a further pressure decrease of 6 divisions. After each change in illumination the system was given some time to reach equilibrium before rate values were again taken.

The rate values obtained are given in table 24 and are shown graphically in figure (23).

TABLE 24/

Fig. 23 a.

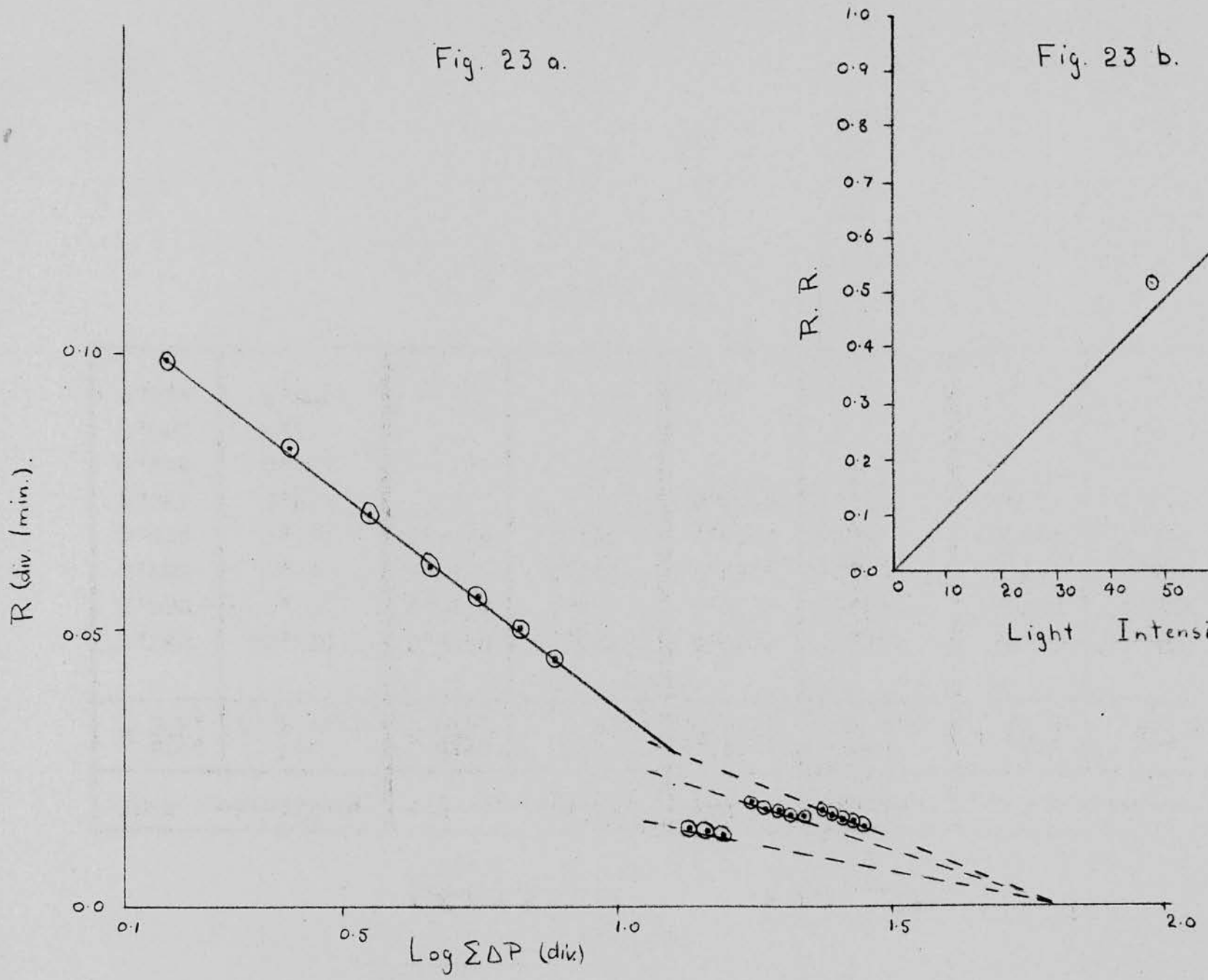


Fig. 23 b.

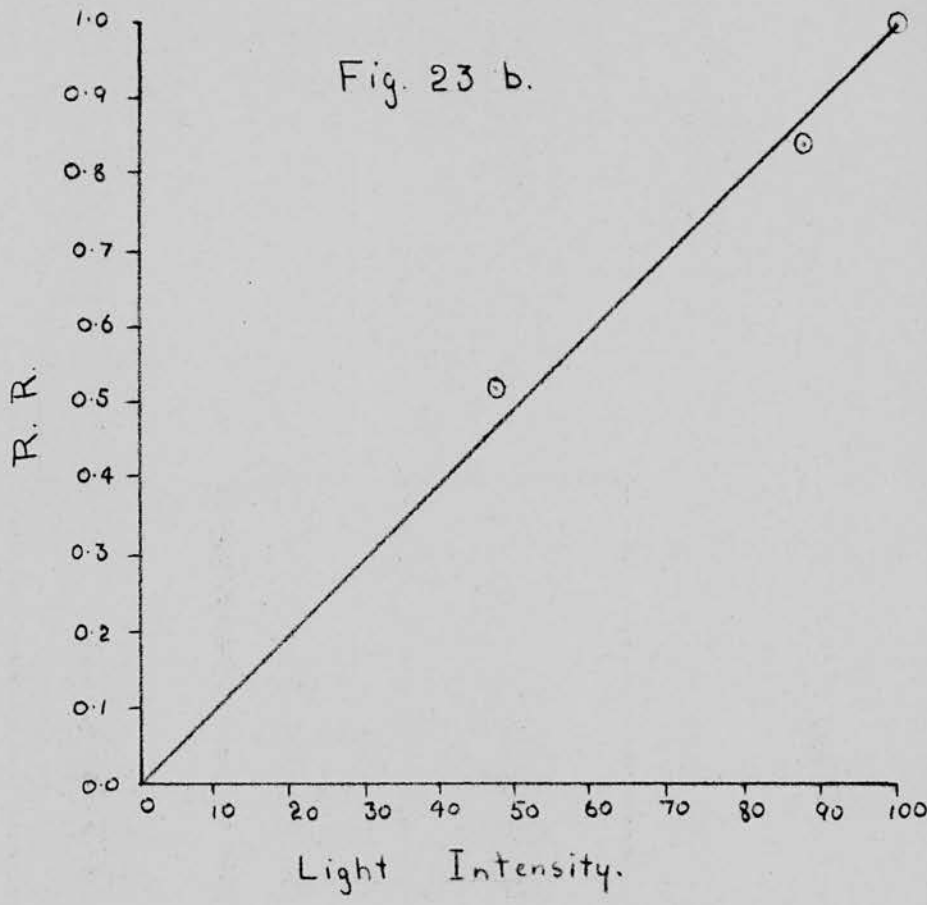


TABLE 24 RUN 13

100% transmission		47% transmission		88% transmission		100% transmission	
R $\frac{\text{div.}}{\text{min.}}$	log ($\Sigma\Delta$P div)	R $\frac{\text{div.}}{\text{min.}}$	log ($\Sigma\Delta$P div)	R $\frac{\text{div.}}{\text{min.}}$	log ($\Sigma\Delta$P div)	R $\frac{\text{div.}}{\text{min.}}$	log ($\Sigma\Delta$P div)
0.143	-0.300	0.0209	1.098	0.0183	1.245	0.0170	1.371
0.098	0.176	0.0138	1.130	0.0173	1.267	0.0160	1.389
0.082	0.398	0.0130	1.162	0.0170	1.290	0.0153	1.406
0.070	0.544	0.0125	1.190	0.0160	1.312	0.0156	1.424
0.061	0.653			0.0160	1.332	0.0140	1.439
0.055	0.740						
0.050	0.812						
0.044	0.875						

From figure 23 it can be seen that the R against $\log \Sigma \Delta P$ line (100%) consists of two linear portions. Using the later portion the relative rates at the various illuminations are as follows.

Transmission %	R.R.
100	1
88	0.84
47	0.52

These values are plotted in figure (23b), which demonstrates the proportionality between the rate of oxygen uptake and the intensity of the incident illumination.

Summary of Oxygen Uptake

When zinc oxide is illuminated in oxygen, photo-:adsorption of oxygen occurs, to a small extent with a commercial sample and to a much greater extent with zinc oxide hyperfine samples, which have a much larger surface area.

The oxygen uptake appears to bear an approximately parabolic relation to time ($\Delta P^2 \propto t$) in its initial stages and eventually becomes approximately exponential ($\Delta P \propto e^{-t}$), while a graph of R against $\log \Sigma \Delta P$ gives linear/

linear portions which can be extrapolated to a limiting value.

Water and carbon dioxide are liberated into the gas phase during illumination, and it would appear that they were originally chemisorbed on the oxide surface.

The rate of uptake depends on pressure and appears to follow a dissociative type Langmuir adsorption isotherm; it is proportional to the intensity of incident light, $\lambda = 3650$ Å light being responsible for a large part of the activation. The rate is also affected by temperature and the apparent activation energy has been obtained.

PHOTO-REACTION OF ZINC OXIDE AND NITRIC OXIDE

In these experiments zinc oxide hyperfine III and nitric oxide prepared as on page (27) were used. When a film of zinc oxide was allowed to stand in an atmos-:phere of nitric oxide a small pressure decrease took place in the dark and a much larger pressure decrease took place on illumination. After this pressure decrease had taken place nitrous oxide was detected in the gas phase and nitrite was detected on the film.

Experiments were carried out, using nitric oxide pressures (initial) of 50 mm (Hg) and 1 mm, approxi-:mately, which will now be described in detail.

1) Using 50 mm (Hg) initial NO pressure

By using an initial pressure of 50 mm the relative decrease in pressure during the reaction becomes in-:significant and a close approximation to isobaric conditions is obtained.

Nitric oxide was admitted to the reaction volume after the zinc oxide film had been pumped at 10^{-4} mm for 5 days. The nitric oxide stood in contact with the zinc oxide in the dark for 200 mins. and the reaction vessel was then illuminated for 10,000 mins. by which time an appreciable pressure decrease had been recorded. The residual gases were pumped through a liquid/

liquid oxygen trap and the contents of the trap were pumped at 10^{-4} mm to remove the last of the NO. The film was washed with water and the nitrite in the washings was estimated using the Griess-Ilosvay reagent.

The results of this experiment are given in table (25) figures 24 and 25 and table (27).

Results/

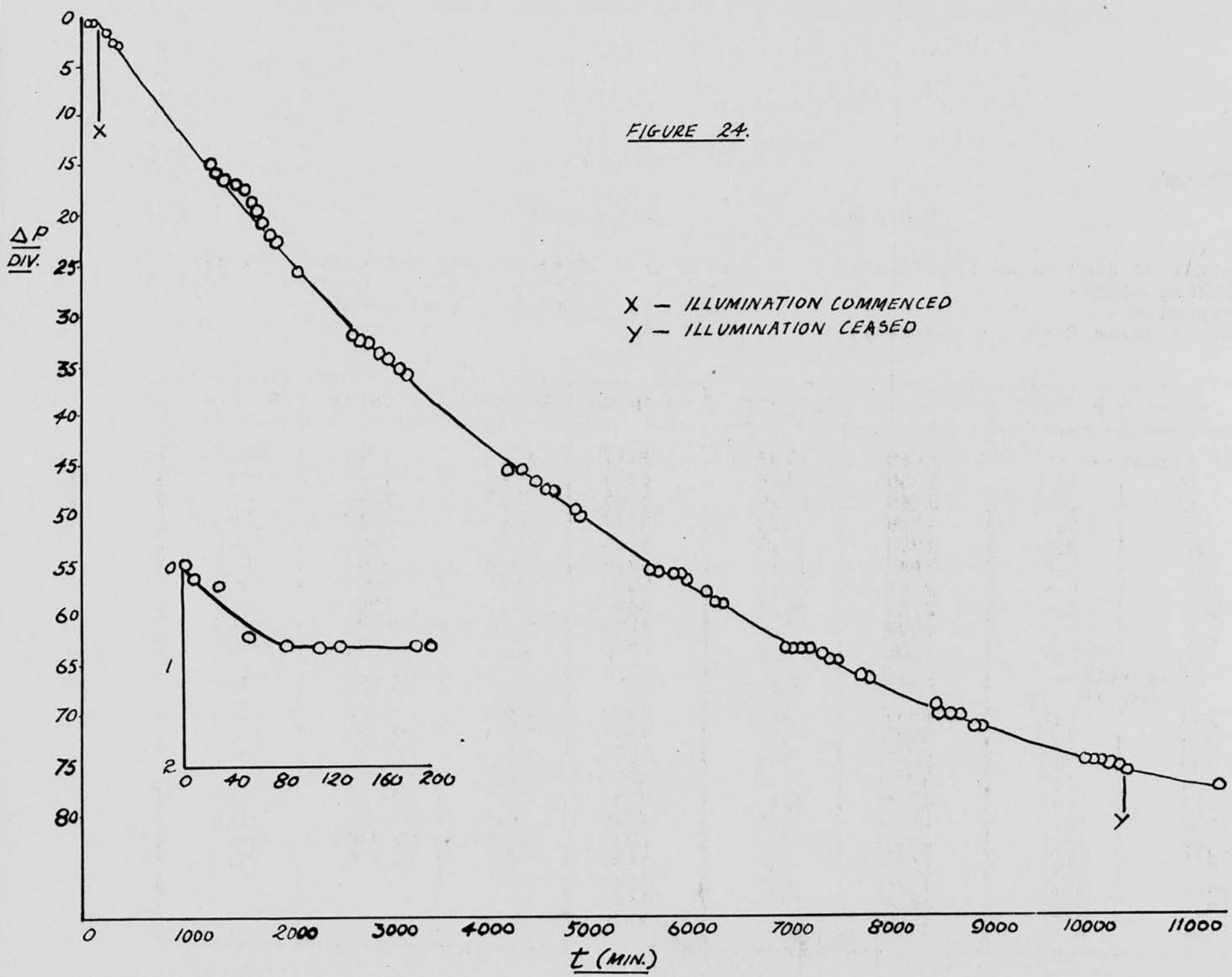

0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
ΔP
DIV.
X
X — ILLUMINATION COMMENCED
Y — ILLUMINATION CEASED
Y
0
1
2
0
40
80
120
160
200
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
t (MIN.)

FIGURE 24.

Results

TABLE 25 RUN 14

Weight of Zinc Oxide Hyperfine III = 0.100 g.
Binding Liquid = Water
Temperature = 25.3° C.
Nitric Oxide Pressure (Initial) = 50 mm (Hg)

Type of Reaction Vessel = IV
Volume of Reaction Vessel = 60.4 ml.
Sensitivity of Gauge = 0.0552 mm/div.

t (mins)	ΔP (div)	t (mins)	ΔP (div)	t (mins)	ΔP (div)	t (mins)	ΔP (div)
no illumination		1640	17.7	4700	47.8	7900	66.7
0	0.0	1700	18.9	4950	49.9	8540	69.3
8	0.1	1745	19.9	4990	50.3	8600	70.3
28	0.2	1798	20.9	5700	55.7	8640	70.3
52	0.7	1882	22.0	5740	55.8	8700	70.3
83	0.8	1945	22.8	5965	56.0	8740	70.3
111	0.8	2150	25.8	6000	56.0	8820	70.3
126	0.8	2735	32.0	6050	56.8	8955	71.3
188	0.8	2795	32.6	6260	57.9	9000	71.3
200	0.8	2900	32.9	6300	58.0	10,075	74.8
illumination commenced		2990	33.8	6360	58.7	10,085	74.8
200	0.8	3055	34.4	6400	59.0	10,150	74.8
253	1.7	3120	34.7	7055	63.6	10,190	74.8
305	2.1	3190	35.7	7115	63.6	10,265	75.3
330	2.7	3250	36.0	7200	63.8	10,325	75.3
380	2.9	4275	45.7	7240	63.8	10,400	75.4
1285	14.9	4348	45.8	7300	63.8	10,445	75.6
1349	15.7	4390	45.9	64.1	standing in dark 17 hrs.		
1405	16.6	4445	46.0	7500	64.7	11,405	77.2
1445	16.7	4548	46.9	7560	64.7		
1500	16.8	4600	47.0	7800	66.2		
1540	17.1	4640	47.7	7840	66.4		

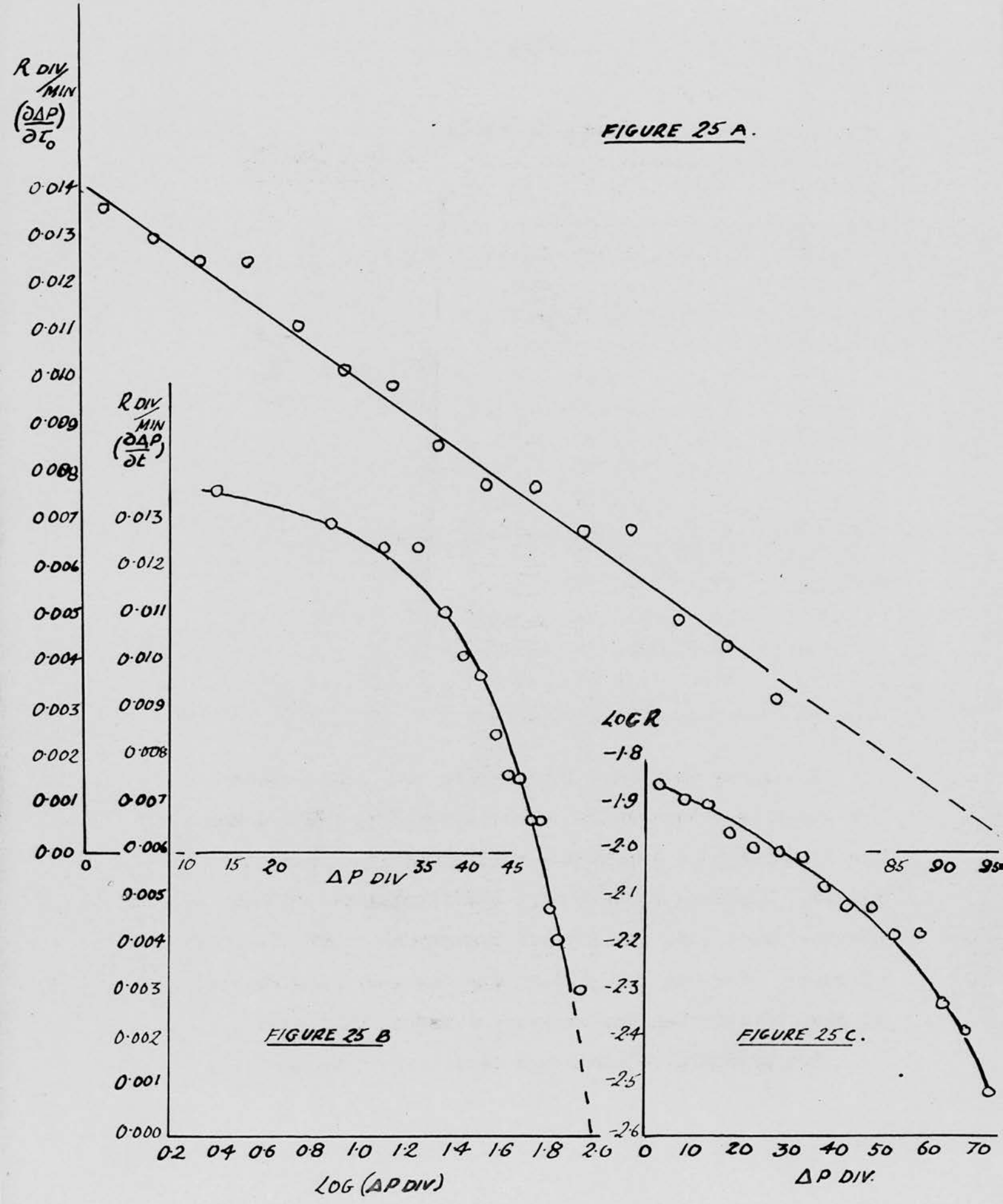


FIGURE 25 A.

FIGURE 25 B

FIGURE 25 C.

TABLE 25 (cont.)

Rates of Photo-Reaction Only

R div/min	$\Sigma\Delta P$ div	log R	$\log\Sigma\Delta P$
0.0137	2.5	-1.863	0.398
0.0130	7.5	-1.886	0.874
0.0125	12.5	-1.903	1.097
0.0125	17.5	-1.903	1.243
0.0111	22.5	-1.955	1.352
0.0102	27.5	-1.992	1.439
0.0098	32.5	-2.009	1.512
0.0085	37.5	-2.071	1.574
0.0077	42.5	-2.114	1.628
0.0076	47.5	-2.119	1.676
0.0067	52.5	-2.174	1.720
0.0067	57.5	-2.174	1.760
0.0048	62.5	-2.319	1.796
0.0042	67.5	-2.376	1.829
0.0031	72.5	-2.509	1.860

ΔP is taken as 0 at t = 200 mins.

Thus ΔP in Rate curves = ΔP in Fig.(24) -0.8

It can be seen from figure (25) that the R against $\Sigma\Delta P$ graph is linear while the R against $\log\Sigma\Delta P$ and the log R against $\Sigma\Delta P$ graphs are smooth curves. The pressure decrease is thus of a different type to that observed when zinc oxide was illuminated in the presence of oxygen (figures 9,10,11). The decrease in pressure is also slower than the decrease observed with oxygen.

The products obtained are described in table (27).

2)/

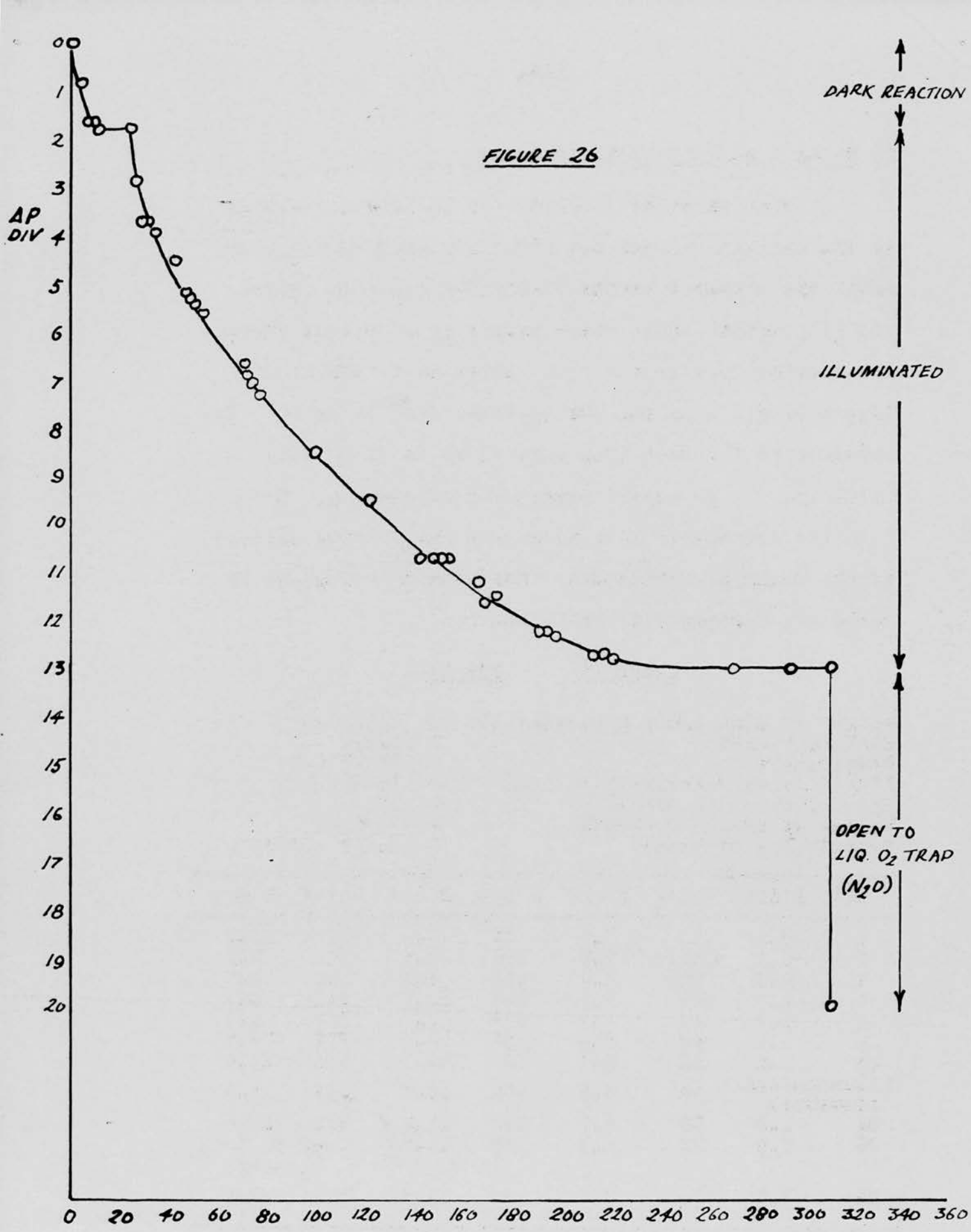


FIGURE 26
ΔP DIV
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
DARK REACTION
ILLUMINATED
OPEN TO LIQ. O_2 TRAP (N_2O)
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360

2) Using 1 mm initial NO pressure

In this experiment about 1 mm of NO was admitted to the reaction volume and after standing in the dark until the pressure became steady the reaction vessel was illuminated until the pressure again became steady. The reaction volume was then opened to an evacuated liquid oxygen trap and the pressure fell to zero. The contents of the cold trap were shown to be nitrous oxide (p.119) by vapour pressure measurements. The film was now washed with water and the nitrite content of the washings estimated. The results are given in table 26, figures (26) and table 27.

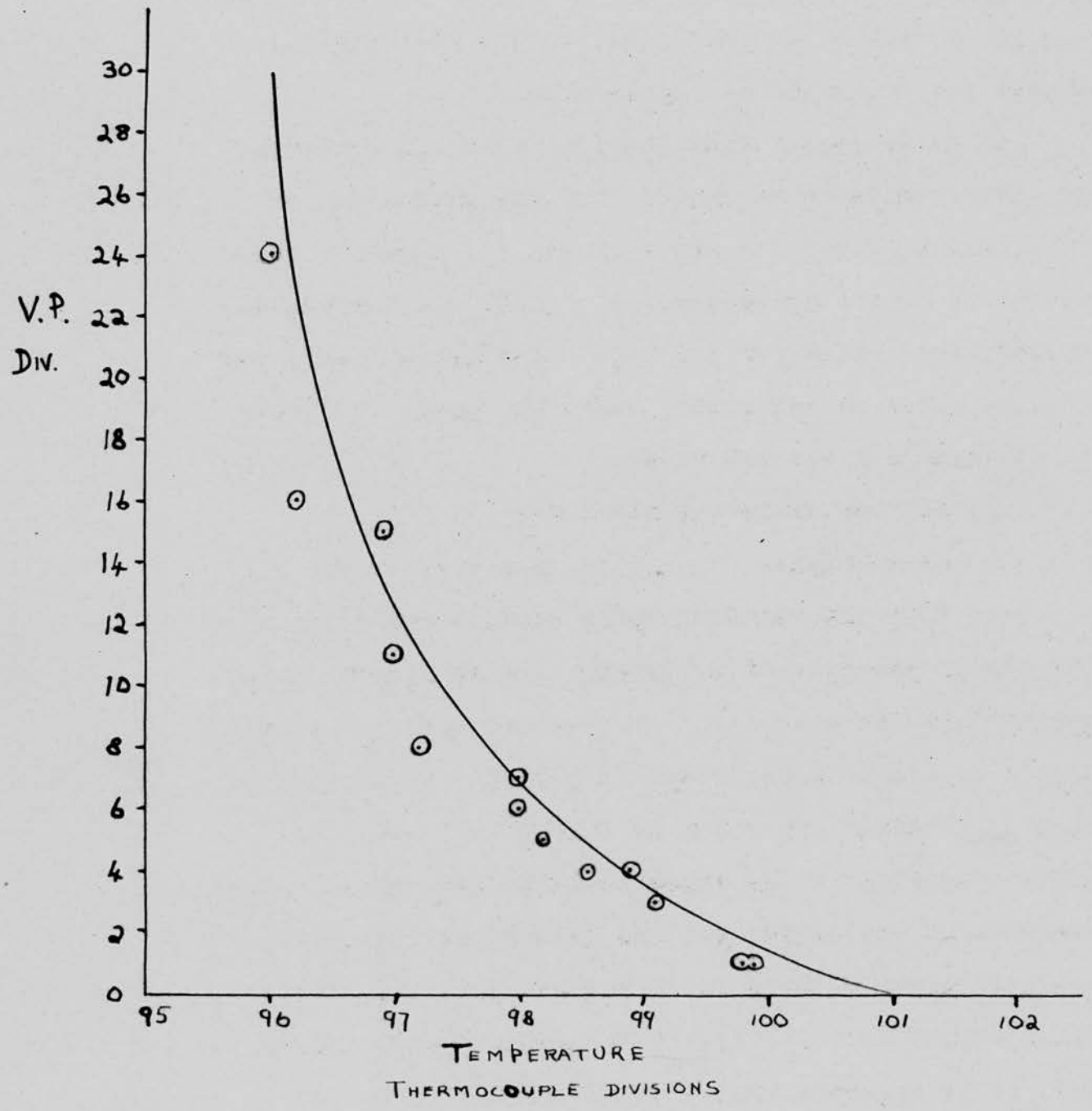
TABLE 26 RUN 15

Weight of Zinc Oxide Hyperfine III = 0.101 g.
Binding Liquid = Water
Temperature = 25.3° C.
Nitric Oxide Pressure (Initial) = 20 div.
Type of Reaction Vessel = IV
Volume of Reaction Vessel = 60.9 ml.
Sensitivity of Gauge = 0.0552 mm/div.

t hrs	ΔP div	t hrs	ΔP div	t hrs	ΔP div	t hrs	ΔP div
0	0.0	30	3.7	77	7.3	191	12.2
2	0.8	33	3.9	100	8.5	194	12.2
4	0.9	34	3.9	122	9.5	198	12.3
6	1.7	46	5.2	143	10.7	214	12.7
8	1.7	48	5.3	147	10.7	218	12.7
10	1.8	50	5.4	150	10.7	222	12.8
24	1.8	52	5.5	153	10.7	270	13.0
illumination commenced		54	5.6	156	10.7	294	13.0
24	1.8	70	6.7	166	11.2	311	13.0
26	2.9	72	6.9	169	11.6	Open to liq. O_2 trap	
28	3.7	74	7.1	173	11.5	311	20.0

It/

Figure 27


V.P.
DIV.
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
95
96
97
98
99
100
101
102
TEMPERATURE
THERMOCOUPLE DIVISIONS

It can be seen from figure (26) that the pressure decrease is due to the removal of nitric oxide but that the production of nitrous oxide in the gas phase re-:duces the magnitude of the decrease.

It would appear that the removal of 20 molecules of nitric oxide is accompanied by the production of 7 molecules of nitrous oxide in the gas phase. The amount of nitric oxide removed ($\sum(NO)$) is therefore approximately equal to $3/2\ \Delta\ P$. Further evidence for this is given in table (27) where the products formed by the reaction are described.

The nitrous oxide was identified by vapour pressure measurements, the vapour pressure of the gas obtained from the reaction space being compared with the vapour pressure of purified cylinder nitrous oxide measured in the same way. The method used to measure vapour pressure is described on page (39) and the results obtained are shown in figure (27) where the continuous line is the experimentally determined vapour pressure of the oxide; and the points are the experi-:mental values obtained with the gas from the reaction space during run (14) described above. From figure (27) it is apparent that the gas obtained from the reaction space was nitrous oxide. The vapour pressure of the gas obtained during run (14) was typical of that found after runs (14 - 16) but could be measured over a greater/

greater temperature range due to the relatively large amount obtained.

Run (16) was similar to run (15); the illumination was not, however, continued until the equilibrium pressure was reached.

TABLE 27/

TABLE 27

Initial NO pressure mm (Hg)	ΔP (total) div.	NO removed ($\frac{3}{2}$ ΔP total) μmoles	N_2O detected μ moles	NO_2^- detected in extract μmoles	Ratio NO:N_2O:NO_2^-
50	77.2	20.70	7.52	6.65	3:1.1:0.9
1.1	13.0	3.58	1.25	0.55	3:1.1:0.5
1	10.8	2.87	0.93	0.60	3:1.0:0.6

No water or carbon dioxide was detected in the gas phase after illumination.

From the final column in table 27 it can be seen that, when the amounts of NO, N_2O and NO_2^- are fairly large, the ratio of $NO:N_2O:NO_2^-$ is approximately 3:1:1. When the amounts are small, as in the last two cases, the ratio of $NO:N_2O$ is still approximately 3:1 but the nitrite detected is only about half that required to give a ratio of 3:1:1 for $NO:N_2O:NO_2^-$.

It is suggested that an error of 0.5 μ moles is involved in the nitrite estimations, and that a ratio of 3:1:1 is the ratio of reactant to products.

It is therefore proposed that the reaction taking place is $3\,NO \rightarrow N_2O + NO_2^-$, with the nitrous oxide being liberated as free gas and the nitrite being adsorbed on the zinc oxide film.

From figure (25a) it can be seen that the rate of reaction R is linearly related to ΔP. This would indicate the concentration of active sites on the surface of the zinc oxide is the rate controlling factor.

It would appear that the dark reaction follows the same course as the photo-reaction, the activation of a large number of sites by illumination being necessary before the reaction will proceed to any appreciable extent.

The/

The reaction will thus be complete when all the active sites are occupied, presumably by nitrite ions trapping the electrons made available by illuminations. From figure (25a) an extrapolated value of $\Delta P_{\infty} = 96.5$ div. at R = 0, i.e. when all the active sites are occupied, is obtained. The reaction would thus be complete when $96.5 \times \frac{3}{2}$ divs. of NO had reacted (25.9 μ moles) giving 8.6 μ moles of nitrite on the surface of the zinc oxide. The total amount of oxygen which can be photosorbed by a similar film is approximately 24 μ moles.

Due to the very small extent of the dark reaction, it has not been possible to examine it in detail.

It is evident that the uptake of nitric oxide with the production of (NO_2^-) on the zinc oxide is kinetically different from the uptake of oxygen. The decomposition of nitric oxide being a surface process may depend on the rate of uptake, as its rate determining step; possible reasons for the difference between uptake of NO and O_2 must include the existence of two types of adsorption centre, either one specific for O_2 and the other for NO, or one at which only oxygen can be adsorbed and one at which NO and O_2 can be adsorbed.

In order to investigate this possibility the following experiment was carried out:-

A film of 0.1 g. zinc oxide hyperfine (III) water bound/

bound in a type IV flask, was illuminated at 25° C. in the presence of 50 mm O_2 until a pressure decrease of 56.3 div. had taken place. The gas phase was withdrawn through a cold trap at liquid oxygen temperature and the amounts of water and carbon dioxide collected were determined in the usual way. 20 mm. of nitric oxide were now admitted to the reaction space and illumination was continued until a pressure decrease of 16.2 div. had taken place. The gas phase was again withdrawn through a cold trap by pumping and the condensable material obtained was identified and the amounts determined. In this case water and nitrous oxide were found, the presence of water being attributed to the previous illumination in oxygen, as none was found when fresh films were illuminated in nitric oxide.

50 mm. of oxygen were again admitted to the reaction space and illuminated until a pressure decrease of 65.7 div. had taken place, when the gas phase was again withdrawn through a cold trap and the water and carbon dioxide obtained was measured.

From the data obtained, ΔP against t curves were drawn and rate values obtained in the usual way. The rates obtained were corrected to allow for the gas phase water and carbon dioxide produced by multiplying them by the total pressure decrease plus the amount of water and carbon dioxide detected over the total pressure decrease, i.e./

i.e. $\frac{\Sigma \Delta P + \Sigma H_2O + \Sigma CO_2}{\Sigma \Delta P}$. ΔP values were similarly corrected, the amounts of water and carbon dioxide detected being small ($<10\%$ Δ P).

The corrected rate values are given below in table (28). The $\Sigma \Delta P$ values for the second oxygen treatment are taken from an initial value equal to the total pressure decrease in the first oxygen treatment i.e. the assumption is made that the uptake of nitric oxide will not affect the oxygen uptake. This assumption is discussed below.

TABLE 28/

Figure 28A

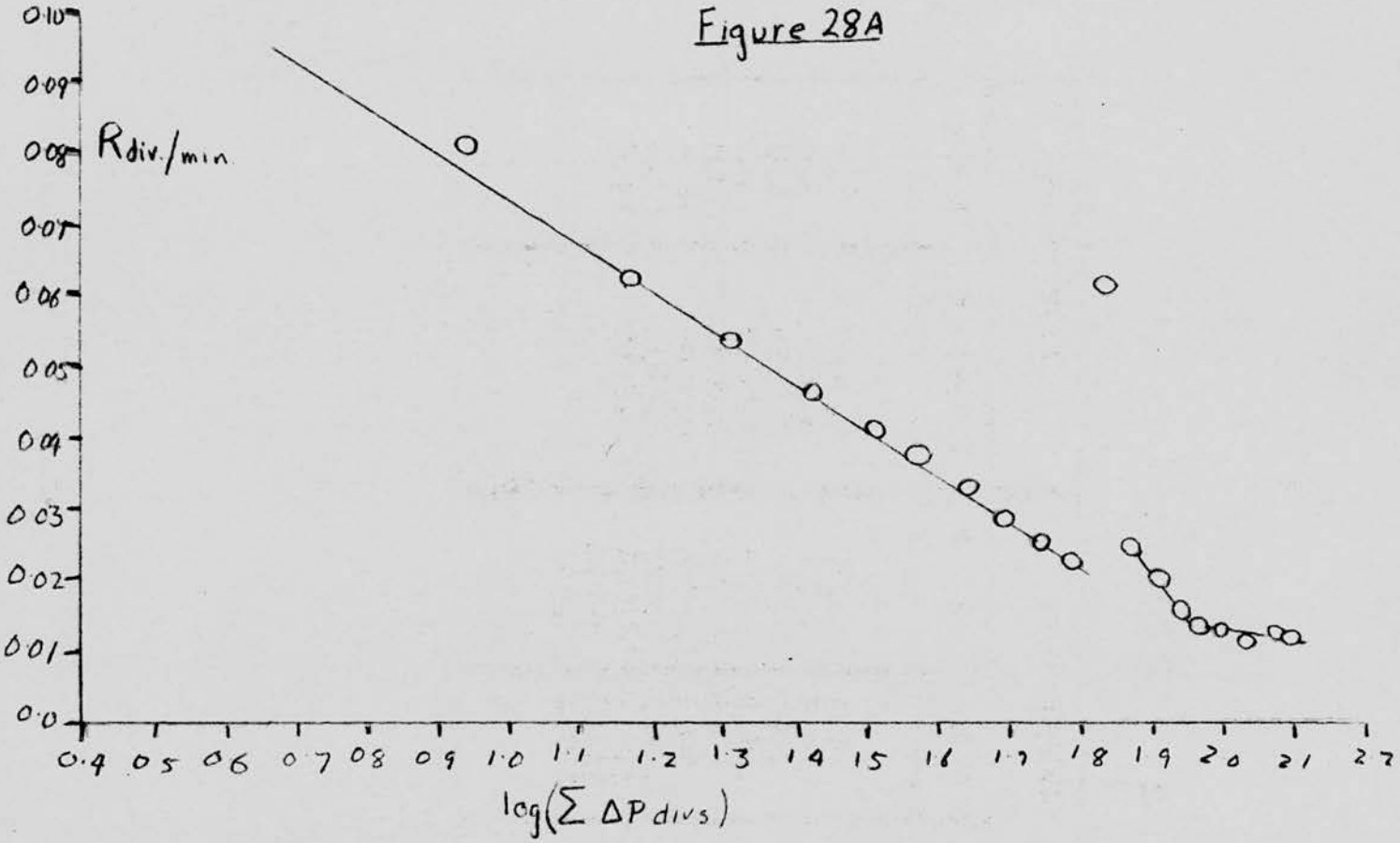


Figure 28B

NO

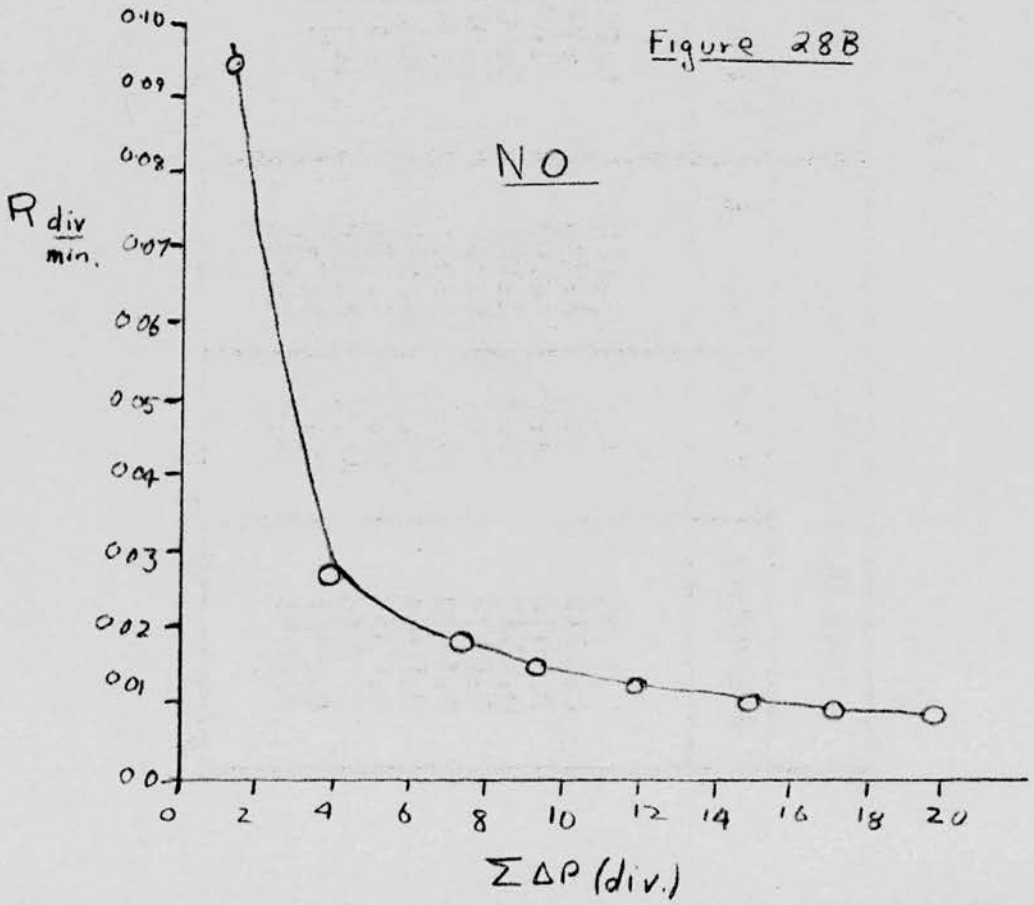


TABLE 28 RUN 17

1st O_2 Illumination			2nd O_2 Illumination			NO Illumination	
R div/min	$\Sigma\Delta P$ div	$\log\Sigma\Delta P$	R div/min	$\Sigma\Delta P$ div	$\log\Sigma\Delta P$	R div/min	$\Sigma\Delta P$ div
0.1160	2.9	0.462	0.0627	68.5	1.838	0.0945	1.3
0.0818	8.7	0.940	0.0251	74.4	1.870	0.0276	3.9
0.0670	14.5	1.162	0.0204	80.7	1.907	0.0180	6.6
0.0542	20.3	1.307	0.0166	86.8	1.938	0.0149	9.2
0.0472	26.1	1.416	0.0144	92.8	1.967	0.0122	11.8
0.0420	31.9	1.504	0.0138	98.9	1.994	0.0103	14.4
0.0384	37.7	1.576	0.0138	106.1	2.027	0.0091	17.0
0.0337	43.5	1.638	0.0136	111.2	2.046	0.0089	19.6
0.0295	49.3	1.692	0.0135	117.3	2.070		
0.0264	55.1	1.741	0.0123	123.4	2.091		
0.0234	60.9	1.785					

In figure (28b), R against log $\Sigma\Delta$ P plots for the oxygen treatment, it can be seen that the result of illumination in nitric oxide is to elevate the rate values on illuminating again in oxygen. Some elevation of rate values would be expected as the film had been subject to two evacuations between the first and second oxygen treatments (see page 59) and this will account for at least part of the observed increase. The nitrite adsorbed on the zinc oxide does not appear to restrict the oxygen uptake, but would, in fact, appear to increase it. As no oxides of nitrogen were detected after this illumination and no nitrate was found on the film when it was washed with water and the washings tested with diphenylamine in concentrated sulphuric acid, however, reaction between oxygen and adsorbed nitrite would appear unlikely.

The effect of previous illumination in oxygen on the nitric oxide uptake was apparently more fundamental than the effect of intermediate nitric oxide treatment on the oxygen uptake. The R against ΔP plot is no longer linear, the rate falling very rapidly during the initial part of the illumination (figure 28a). As the reaction would appear to be the same as with a fresh film, on the basis of the nitrous oxide obtained, the most likely explanation would seem to be that the adsorption centres for nitric oxide are involved in oxygen/

oxygen uptake and inhibited, while the adsorption of nitrite does not inhibit the uptake of oxygen, due either to the formation of an alternative centre or vacation of the nitric oxide adsorption centre by the nitrite formed.

Due to the slow rate of the nitric oxide decomposition it was not possible to investigate the effect of change of pressure on the rate of decomposition.

Summary

When NO is admitted to a zinc oxide film a small dark uptake of NO is observed. On illumination a larger decrease in pressure was observed the rate of which was linearly related to the amount of nitric oxide adsorbed. N_2O was detected in the gas phase and nitrite was detected on the zinc oxide in amounts which correspond to the equation.

$$3\ NO + e = \underset{(gas)}{N_2O} + \underset{(adsorbed)}{NO_2^-}$$

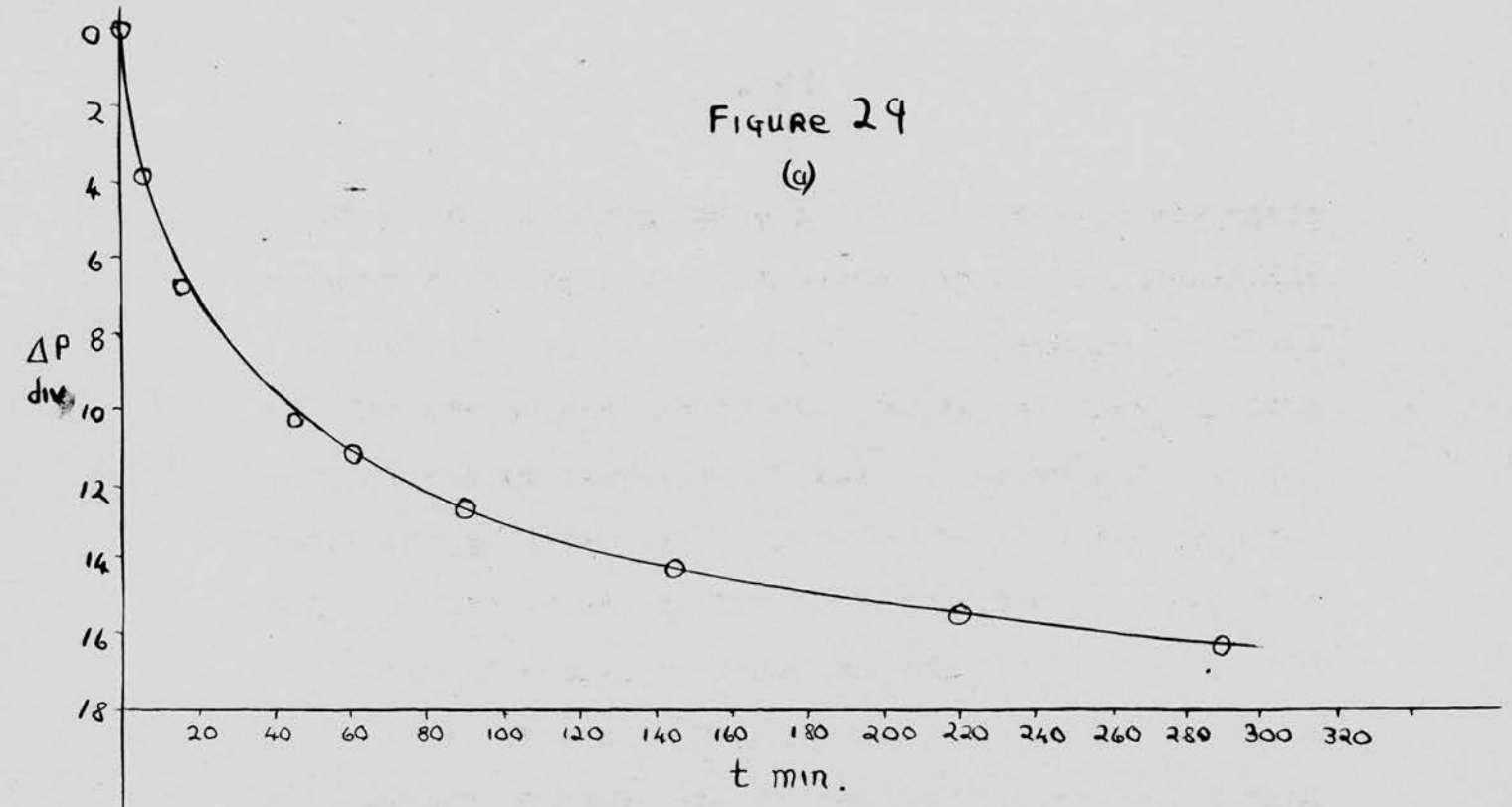
Illumination of the zinc oxide in oxygen prior to illumination in nitric oxide would appear to inhibit the adsorption of NO, while treatment of zinc oxide with nitric oxide has no marked effect on the uptake of oxygen.

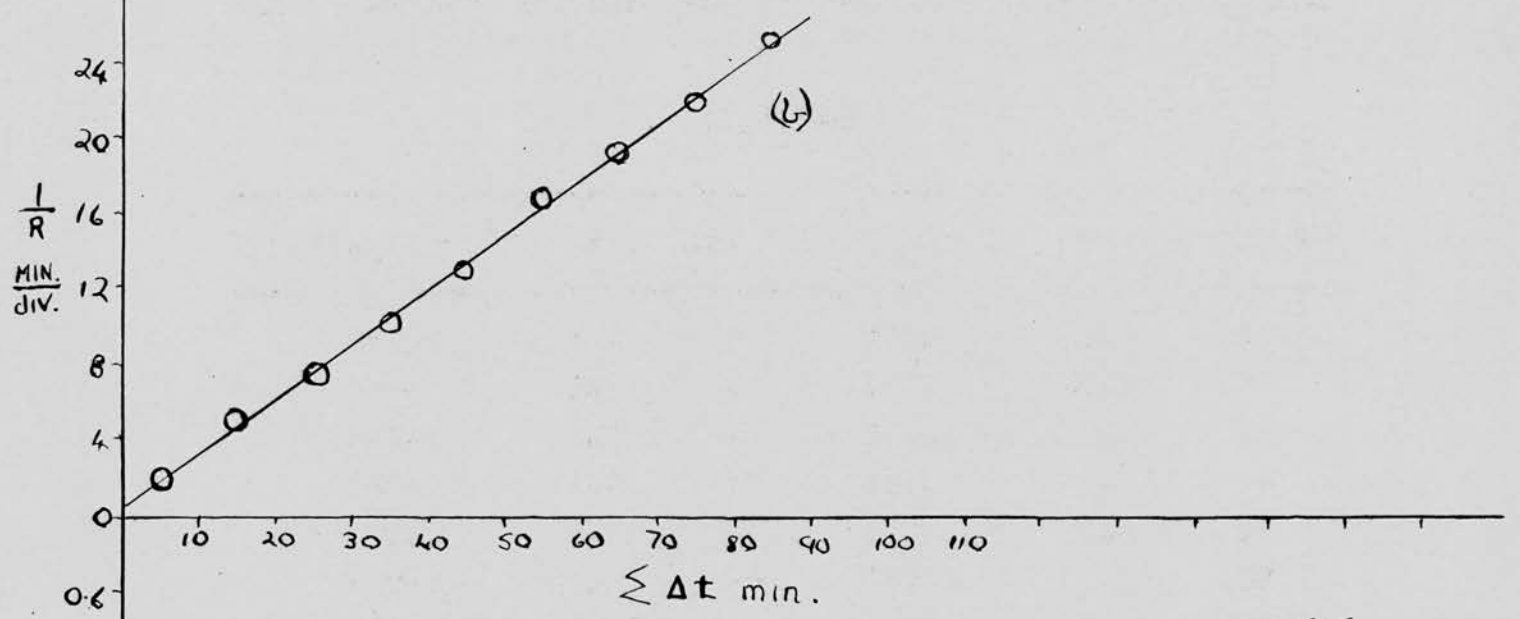
DARK UPTAKE OF AMMONIA BY ZINC OXIDE HYPERFINE

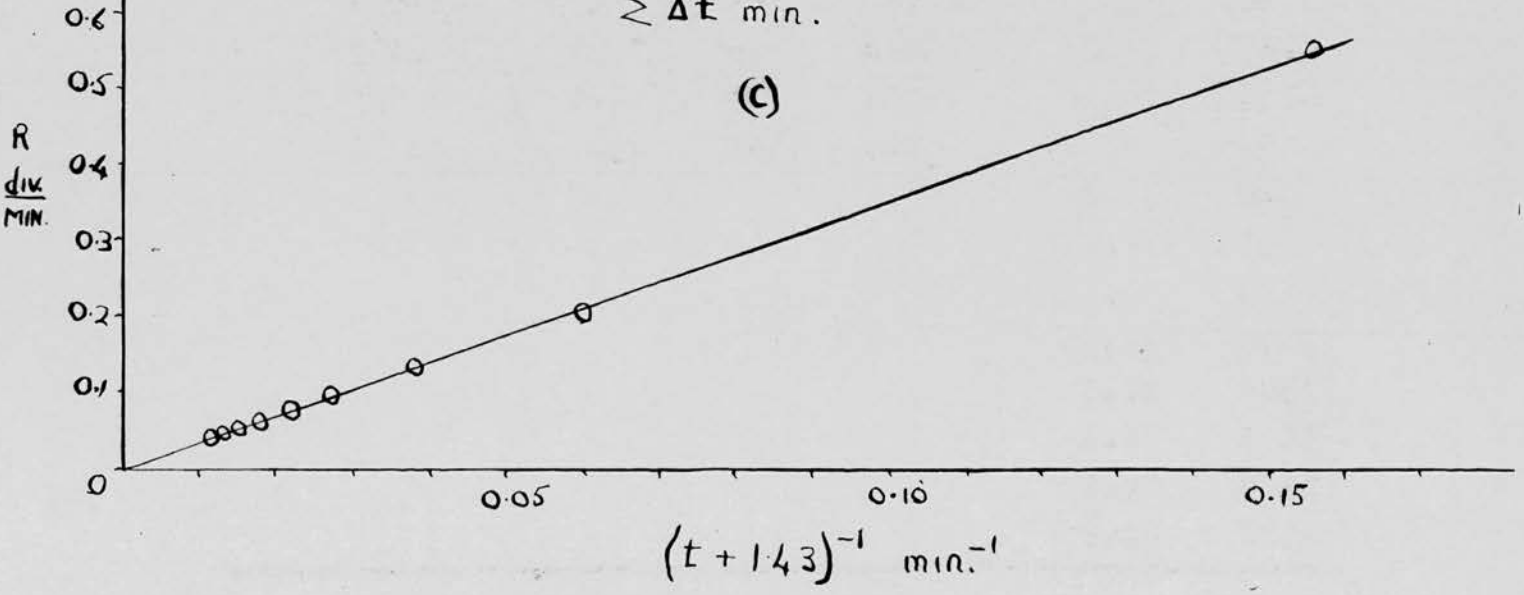
A film of zinc oxide hyperfine, after the usual evacuation, adsorbed ammonia gas in the dark, at the same time desorbing water. Part of the ammonia adsorbed, was desorbed again, when the system was subse-:quently evacuated, together with a further amount of water. The following experiments were carried out to determine how much ammonia a zinc oxide film could adsorb, what part of the adsorbed ammonia was held irreversibly and how much water was liberated as a consequence of the ammonia adsorption.

A film of 0.100 g. zinc oxide hyperfine was pre-:pared in a type IV flask and the usual evacuation was carried out. 20 mm. of ammonia were rapidly admitted and the decrease in pressure during the next 36 hours was noted, a virtually steady pressure being reached by that time. ΔP , t and R values are given in table (29) and Figure (29a) shows the initial part of the fall in pressure with time during the dark uptake of ammonia. The gas phase was now rapidly withdrawn by allowing it to come into contact with a cold trap at liquid oxygen temperature, the time required to reduce the pressure to 0.1 mm being leas than 2 mins. The gas phase obtained in this way consisted of water and ammonia which were separated by distillation at -62° C. and the amount of water/

FIGURE 29


(a)
ΔP div.
0
2
4
6
8
10
12
14
16
18
20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320
t min.


(b)
1/R MIN./DIV.
0
4
8
12
16
20
24
10 20 30 40 50 60 70 80 90 100 110
Σ Δt min.


(c)
R div./MIN.
0
0.1
0.2
0.3
0.4
0.5
0.6
0.05
0.10
0.15
(t + 1.43)⁻¹ min.⁻¹

water was measured. It is possible that during the withdrawal of the gas phase some desorption of water or ammonia from the film, took place; it is considered, however, that any error introduced in this way will be small. The amount of ammonia adsorbed by the film was taken as the pressure decrease observed plus the amount of water detected as above, plus a correction to allow for the amount of ammonia taken up before it was possible to read the Bourdon gauge i.e. while the ammonia was being admitted to the reaction space. This

TABLE 29

t min	ΔP div	R div/min	t min	1/R	$1/(T + 1.43)$
0	0.0	0.550	5	1.8	0.156
5	3.8	0.200	15	5.0	0.061
14	6.8	0.135	25	7.4	0.038
44	10.3	0.099	35	10.1	0.027
60	11.2	0.076	45	13.3	0.022
90	12.7	0.060	55	16.7	0.018
145	14.2	0.052	65	19.2	0.015
220	15.6	0.046	75	21.8	0.013
290	16.3	0.040	85	25.0	0.0116
340	17.0				
407	17.7				
1360	21.6				
1500	22.0				
1585	22.0				
1665	22.1				
1840	22.6				
2106	24.6				

amount/

amount was estimated to be 7.1 div. by the following method:-

Rate values (R) were calculated from figure (29a) by dividing the pressure drop over equal intervals of time by the time interval (10 min). The reciprocals of the rates were then plotted against the time elapsed at the middle of the time interval ($\Sigma\Delta t$); the plot obtained is shown in figure (29b). It can be seen that a linear relationship exists between the rate R and the elapsed time Δt which can be represented by the equation:-

$$\frac{1}{R} = K_1 t + K_2 \qquad (1)$$, where K_1 and K_2 are constants. This is one form of the Roginsky-Zeldovich type of equation for chemisorption

$R = ae^{-bq}$ where q is the amount adsorbed and R is dq/dt, and it appears that the pressure decrease observed follows this equation, at least over the initial stages.

Rearrangement of equation (1) gives

$$K_1 R = \frac{1}{t + \frac{K_2}{K_1}} \qquad (2a)$$

values of K_1 and K_2 being obtainable from figure (29b). The value of t was taken as zero, however, when the first gauge reading was taken and a correction must therefore be made to allow for the time during which the ammonia was admitted to the reaction space. It is believed that the K_2/K_1 term in the above equation represents/

represents this correction term, being slightly less than the actual time involved, while the pressure was steadily rising during this time.

The values for K_1 and K_2 obtained from figure (29b) were

$$K_1 = 0.281 \qquad K_2 = 0.41$$

thus $K_2/K_1 = 1.43$ mins.,

and $$R = \frac{3.56}{t + 1.43} \text{ divisions/min} \qquad .....(2b)$$

Figure (29c) demonstrates that a linear plot is obtained when R is plotted against $(t + 1.43)^{-1}$. The rate over the first 1.43 minutes can now be obtained by substituting $t = -0.715$ in (2b) giving

$$R = 4.96 \text{ div/min.}$$

but $$R = \frac{d\Delta P}{dt}$$

therefore $d\Delta P = 4.96 \times 1.43 = 7.1$ div.

The actual time taken to admit the ammonia was 2 min. and, from the above, the pressure change occurring during that time is taken as 7.1 divisions.

The film now stood in contact with a cold trap at liquid oxygen temperature for 12 hours, and the contents of the cold trap at the end of this time were examined. Ammonia and water were the only substances detected and the amount of ammonia obtained was subtracted from the amount of ammonia previously adsorbed by the film to give/

give the amount of ammonia irreversibly held. That it was irreversibly held was shown by allowing the film to stand in contact with the cold trap for a further 12 hours at the end of which time, some water but no ammonia was detected.

This sequence of operations was carried out every 48 hours. With each treatment the rate of pressure decrease was initially of the same order, but the rates fell off with time more sharply with each successive treatment. For each treatment a correction was made for the initial adsorption occurring during addition of ammonia in the way described above.

For example, 20 mm ammonia (= 362 divisions) were initially added; after 36 hours the pressure had fallen to the almost steady value of 337.4 divisions. With-:drawal of the gas phase at this stage showed that 16.6 divs. of water had been liberated; the correction made to allow for the adsorption of ammonia taking place during the admission of ammonia was 7.1 divs. Thus 48.3 divisions of ammonia had been adsorbed. After 12 hours in vacuo in contact with the cold trap, the amount of ammonia obtained was 1.7 div. and the water obtained was 1.8 divisions the film now holding 46.6 div. ammonia and the total water liberated being 18.4 divs.

The results were as follows:-

Figure 30(a)

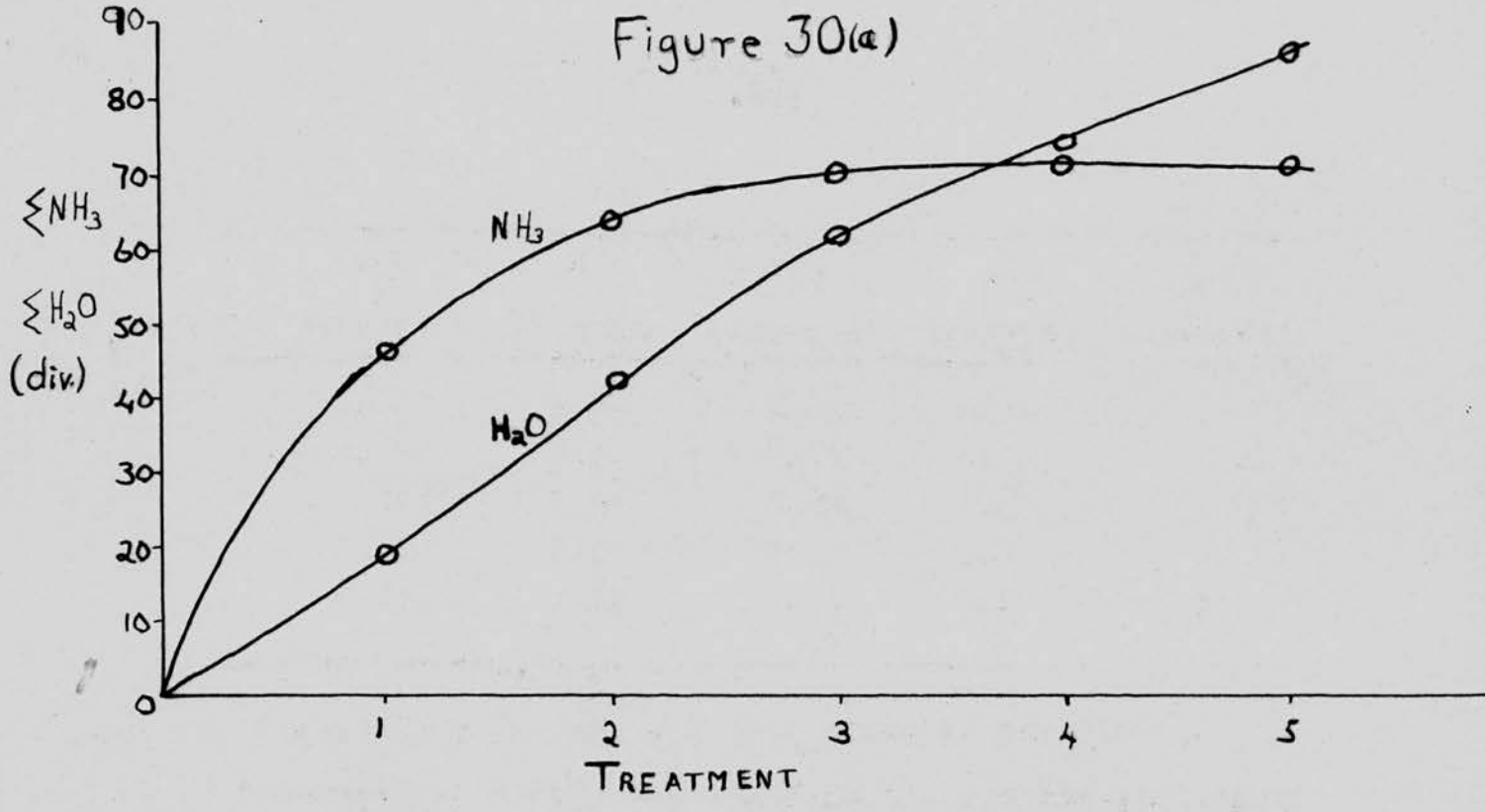
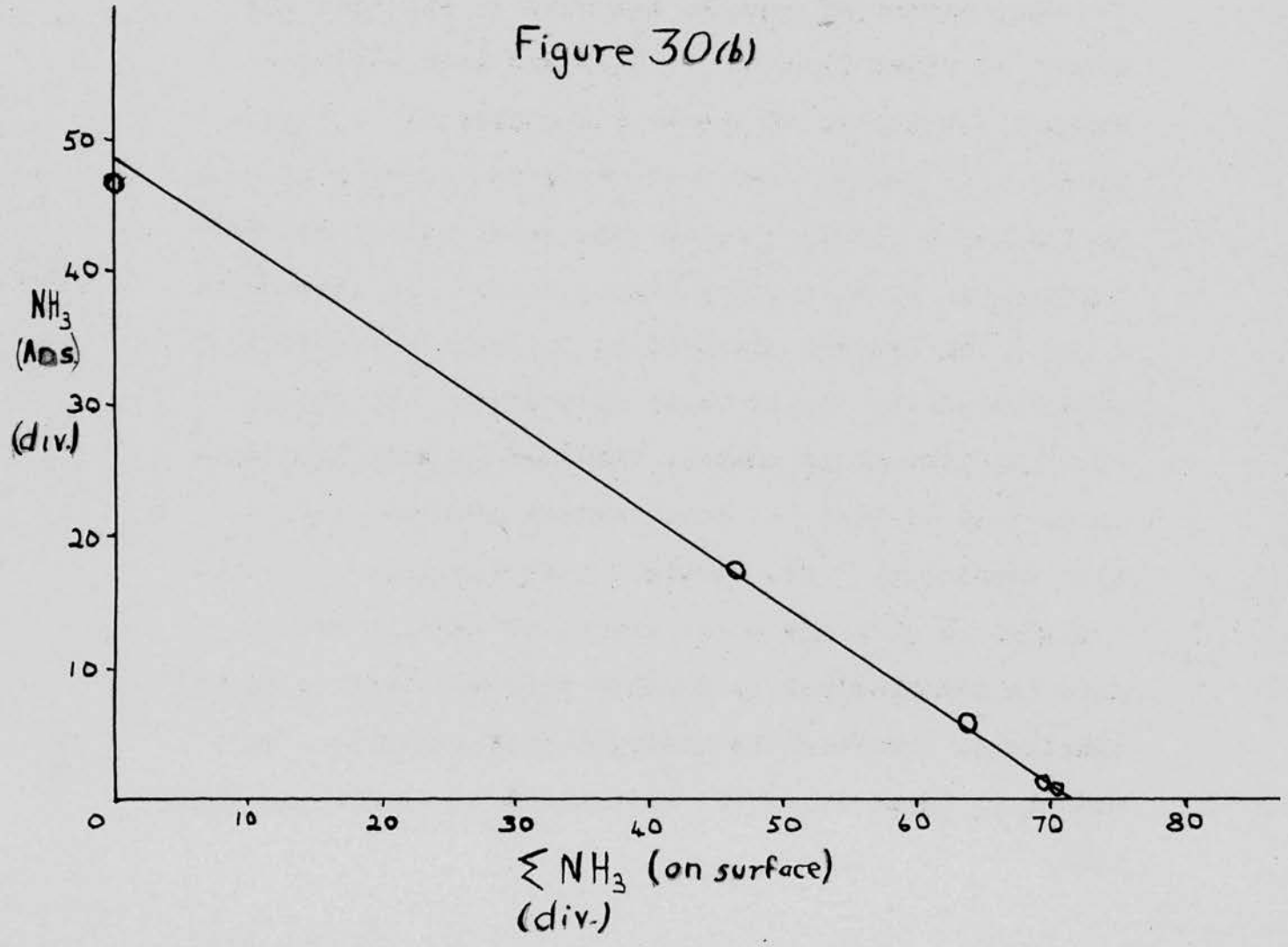


Figure 30(b)



NH_3 Treatment	NH_3 (div) adsorbed	H_2O (div.) recovered	ΣNH_3 (div) adsorbed	ΣH_2O (div.) recovered
1	46.6	18.4	46.6	18.4
2	17.2	24.7	63.8	43.1
3	5.7	18.3	69.5	61.4
4	1.0	11.9	70.5	73.3
5	0.6	12.6	71.1	85.9

On standing in contact with a cold trap at liquid oxygen temperature for 12 hours subsequent to treatment 5, 10.4 divs. of water was obtained.

The amount of ammonia adsorbed (ΣNH_3) and the amount of water desorbed (ΣH_2O) are both plotted against the number of treatments undergone in figure (30a). It can be seen that while the ammonia adsorbed approaches a limiting value, the water desorption is represented by a steadily rising line. At treatments 4 and 5 the ammonia adsorbed is in approximate unit molecular ratio to the water recovered. In figure (30b) the amount of ammonia adsorbed in each treatment is plotted against the total amount adsorbed before that treatment. The straight line obtained is extra-:polated to give the total amount of ammonia which must be adsorbed before further treatment will give no additional irreversible adsorption of ammonia. This amount is taken to be the saturation value for the film, that/

that is, the amount of ammonia required to cover all available adsorption centres. This value is 71.2 div. (12.7 μ moles).

From the irreversible nature of this adsorption and the obedience of the rate of adsorption to the Roginsky-Zeldovich equation, this process was considered to be one of chemisorption.

The water liberated during the ammonia treatment showed a gradual drop in rate of desorption from treatment to treatment, with occasional higher values. The water was apparently produced in the gas phase during the ammonia treatment as it is thought unlikely that any appreciable amount of desorption from the glass or zinc oxide would have taken place during the rapid removal of the ammonia. The water obtained on standing in contact with the cold trap is obviously produced by desorption from the zinc oxide and/or the walls of the apparatus. The amount of water obtained overall is compared with the amount obtained on pumping and standing in contact with a liquid oxygen cooled cold trap from a zinc oxide film of the same weight which had been given the usual initial evacuation (see page 62).

Average rate of water production during NH_3 treatments

= 0.640 μ moles/hr/g.

Average/

Average rate of water production with fresh film

= 0.56 μ moles/hr/g.

The similarity of these figures suggests that only water liberated in the same way as for an untreated film is obtained during treatment with ammonia. The appearance of this water in the vapour phase, however, would indicate a possible adsorption of ammonia on centres previously occupied by water, as the water has, apparently, a higher vapour pressure in presence of ammonia than when a film stands in vacuo.

ILLUMINATION OF AMMONIA TREATED FILMS IN OXYGEN

Two experiments were considered and values of ΣO_2 obtained from extrapolations of R against log $\Sigma \Delta P$ curves were used.

In the first experiment, run (17), a fresh film of zinc oxide hyperfine 0.100 g. was given the usual evacuation and then treated with ammonia as in the preceding section until the film had taken up at least 99% of its total irreversibly adsorbed ammonia (observed uptake 71 div. extrapolated total uptake 71.2 div. see page 135). The reversibly adsorbed ammonia was removed by allowing the film to remain in contact with a cold trap at liquid oxygen temperature until no further desorption occurred. The film was then illuminated in 50 mm. oxygen and pressure and time readings were taken and plotted to give an isotherm from which rate values were calculated in the usual way. The rate values were plotted against log $\Sigma \Delta P$ and the curve obtained which was linear in its later stages was extrapolated to give a value for $\Sigma \Delta P_\infty$ at R = 0. The gas phase was withdrawn rapidly after the illumination, the pressure dropping to 0.1 mm. in approximately 2 mins.; it was assumed that in this time no desorption took place from the film or vessel walls and that the products obtained, which were collected by passing the gas/

gas through a cold trap immersed in liquid oxygen had been present in the gas phase (p.79). The products so obtained were measured and identified in the usual way, and the amount obtained was added to the pressure decrease observed, $\Sigma\Delta P$, to give the total oxygen uptake $\Sigma(O_2)$ and $\Sigma(O_2)_\infty$, the uptake which would occur in infinite time was calculated as $\Sigma(O_2)_\infty = \frac{\Sigma(O_2)}{\Sigma\Delta P}\cdot\Sigma\Delta P_\infty$. The assumption has been made here that all the products of reaction are condensable at liquid oxygen temperature.

In the second experiment (run 18) a fresh film of 0.100 g. zinc oxide hyperfine was illuminated in oxygen after the usual evacuation and the value of $\Sigma(O_2)_\infty$ was obtained as above. The film was now treated with ammonia as above and subsequently illuminated in 50 mm. oxygen, a new $\Sigma(O_2)_\infty$ value being obtained. The ammonia treatment and illumination in oxygen were now repeated to give a third $\Sigma(O_2)_\infty$ value. The rates obtained and the R against log ΣO_2 graphs are given in table (30) and figure (31). The ΔP values observed have been corrected throughout to give $\Delta(O_2)$ by the following formula:-

$$\Delta(O_2) = \Delta P \times \frac{[\Sigma\Delta P + \Sigma H_2O + \Sigma CO_2]}{\Sigma\Delta P}$$

when $\Sigma\Delta P$, ΣH_2O and ΣCO_2 are the total observed pressure decrease, and the amounts of water and carbon dioxide/

dioxide detected in the gas phase, respectively. The initial part of these rate curves have been omitted, the latter, linear, portion only being shown here.

TABLE 30/

FIGURE 31

(a)

Run 17

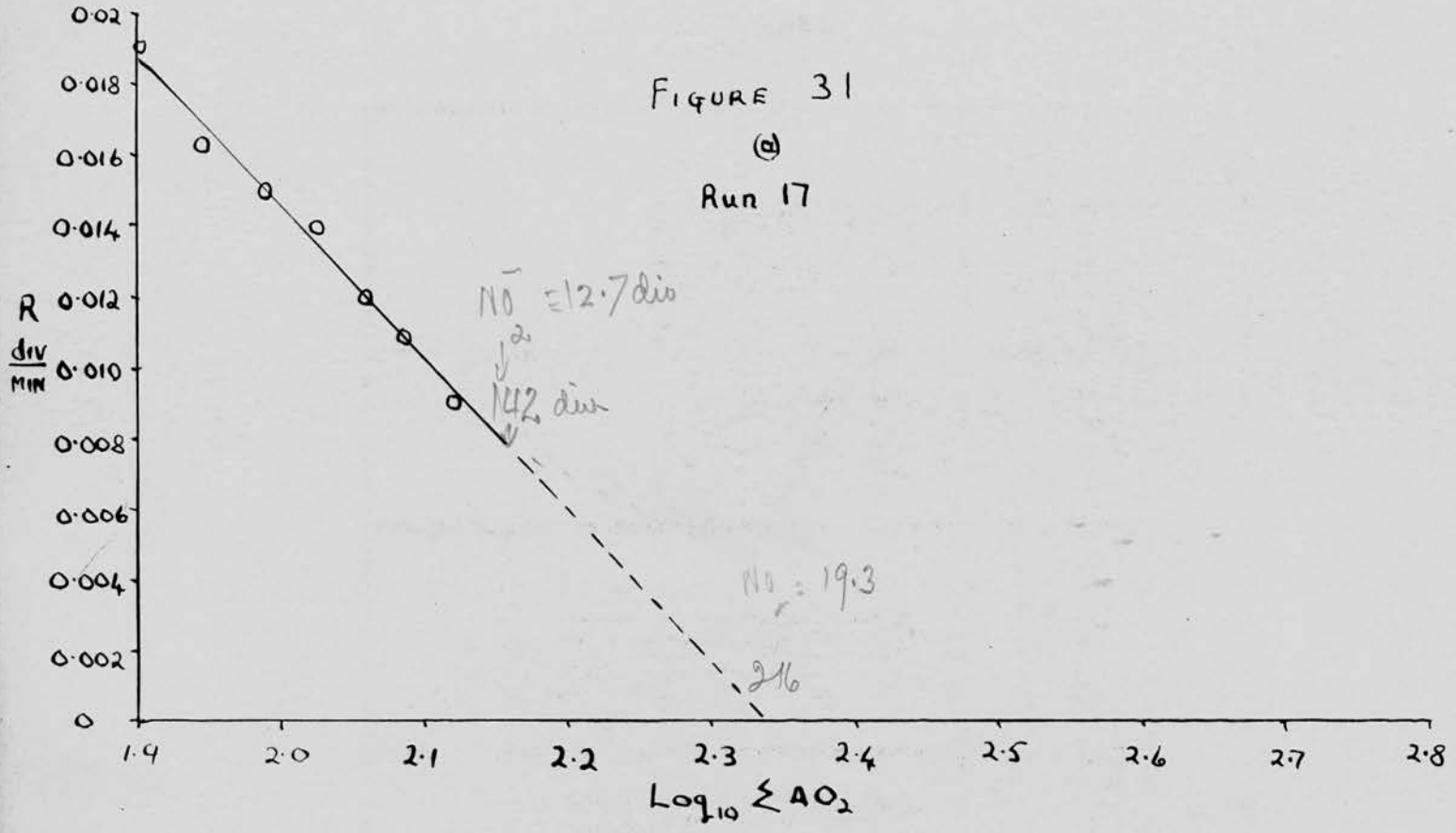


FIGURE 31

(b)

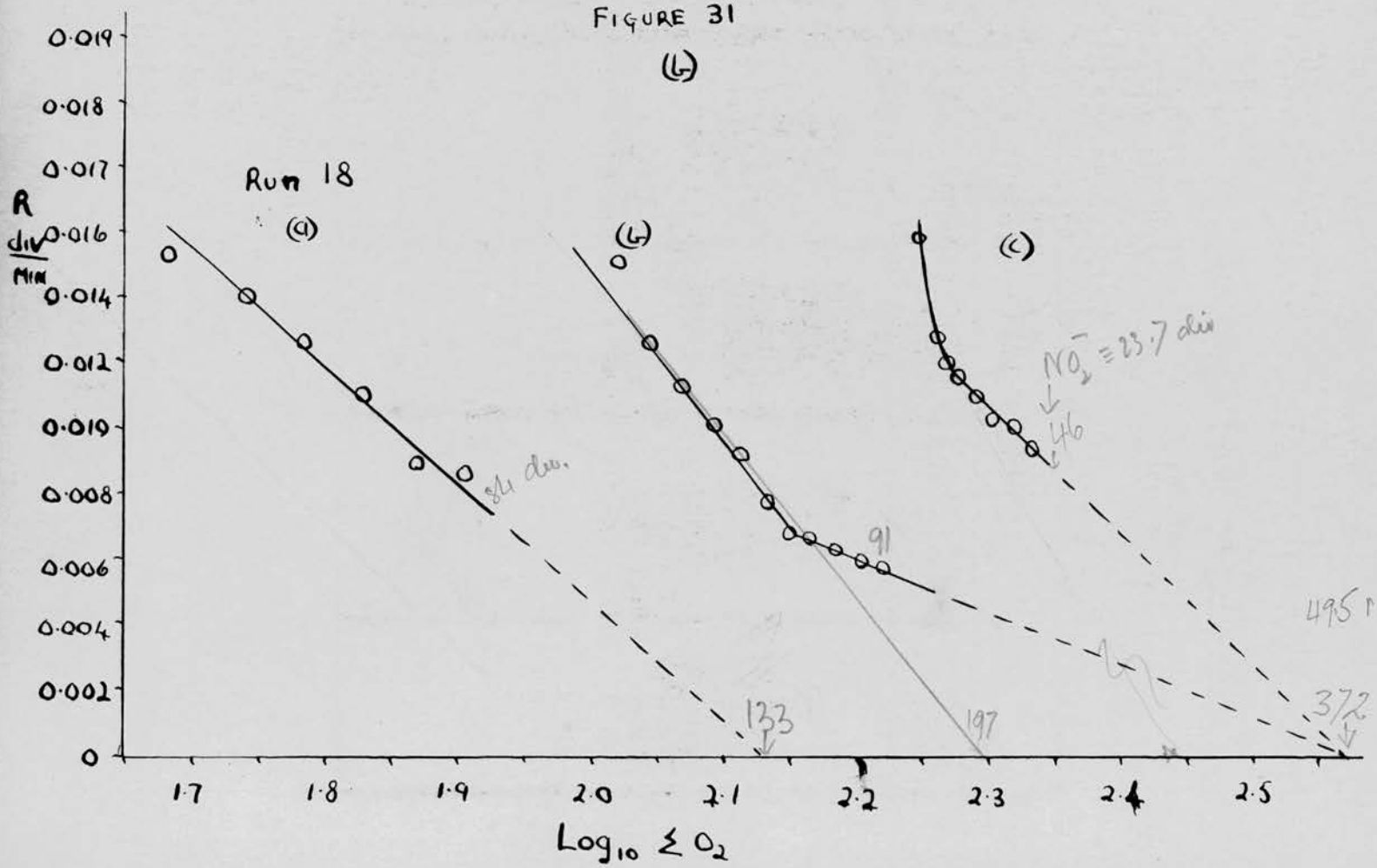


TABLE 30

Run 17		Run 18(a) 1st O_2 treatment		Run 18(b) 2nd O_2 treatment		Run 18(c) 3rd O_2 treatment	
R div/min	log $\Sigma\Delta(O_2)$	R div/min	log $\Sigma\Delta(O_2)$	R div/min	log $\Sigma\Delta(O_2)$	R div/min	log $\Sigma\Delta(O_2)$
0.0192	1.905	0.0153	1.682	0.0331	1.934	0.0157	2.248
0.0163	1.948	0.0140	1.736	0.0240	1.964	0.0126	2.263
0.0149	1.988	0.0125	1.784	0.0196	1.992	0.0115	2.278
0.0139	2.024	0.0109	1.827	0.0150	2.019	0.0109	2.292
0.0119	2.057	0.0089	1.866	0.0125	2.044	0.0102	2.306
0.0108	2.088	0.0085	1.903	0.0112	2.069	0.0099	2.320
0.0089	2.117			0.0100	2.091	0.0093	2.335
Final	=84.1 div	Final	=65.9 div	0.0091	2.112	Final	=28.7
at t	=122 hrs.	at t	=82 hrs.	0.0076	2.132	at t	=69 hrs.
				0.0067	2.153		
				0.0065	2.171		
				0.0062	2.188		
				0.0058	2.206		
				0.0056	2.224		
				Final	=72.8		
				at t	=167 hrs.		

It can be seen from figure (31b), that a break occurs in the R against log $\Sigma\Delta(O_2)$ plot during the second illumination in run 18(b) while no such break occurs in the same plot for run 17. It is considered however that had run 17 been continued, such a break would have appeared. The similar nature of these plots up to the point where log $\Sigma\Delta O_2$ = 2.1 allows a comparison of the amounts of oxygen taken up, in the same time, during run 17 and the first two oxygen treatments in run 18, to be made. This comparison is shown below:-

The 18(a) run (no ammonia pretreatment) will not show a corresponding break: the extrapolated value is the normal figure.

<u>After 15 hours</u>

Film (17)	= 96.4 div. oxygen
Film (18) before NH_3 treatment	= 68.5
Film (18) after NH_3 treatment	= 46.3
Film (17) total	= 96.4
Film (18) total	= 114.8
Difference	= 18.4 div. (= 19% increase on film (17) value)

<u>After 50 hours</u>

Film (17)	= 118 div. oxygen
Film (18) before NH_3 treatment	= 84
Film (18) after NH_3 treatment	= 60

Film/

Film (17) total	= 118
Film (18) total	= 144
Difference	= 26 (= 22% increase on film (17) value)

Extrapolation of the R against $\log \Sigma\Delta O_2$ line for run 17 and the initial portion of this line for the second oxygen treatment in run 18 gives the following results.

Run 17 extrapolation	$\Sigma\Delta(O_2)_\infty$ = 216 div.
Run 18 extrapolation	$\Sigma\Delta(O_2)_\infty$ = 191 div.
Difference	= 25 div (= 11.6% decrease on film (17) value)

In each case, for illuminations of 15 or 50 hrs., the oxygen uptake for an ammonia treated surface is always greater than that for an untreated surface, presumably due to oxidation of ammonia. It is also to be noted that ammonia treatment of a surface largely pre-oxidised (the ratio of the actual oxygen uptake to the final extrapolated possible value (18a) is 0.67), leads to a subsequent rate of ammonia uptake approxi-:mately equal to the initial oxygen uptake; at the same time the 15 hrs. subsequent illumination produces a total oxygen uptake which suggests that the oxygen uptake and the ammonia-oxygen reaction sites are largely independent. The 19% increase at t = 15 hrs. is not surprising in that further oxygen (independent) uptake/

uptake is then expected, but one would predict at 50 hrs. a smaller percentage increase. It can only be suggested here that the ammonia reaction is essen-:tially faster and is approaching its infinity value more quickly. While there is here an 11% difference, it can be said that the prior photo-uptake has not essentially altered the amount of oxygen taken up initially in the ammonia-oxygen reaction.

From figure (31b) it can be seen that when film 18(b) was treated with ammonia, subsequent uptake of oxygen occurred at an enhanced rate, the R against log $\Sigma\Delta O_2$ becoming linear after a short initial period during which a very steep drop in rate was observed. Extra-:polation of the linear portion of this line and extra-:polation of the final portion of the rate curve for the previous illumination (run 18b) give the same value of $\Sigma\Delta(O_2)_\infty$ = 133 div., the uptake observed being 67% of this figure. On the basis that photoadsorption of oxygen and oxidation of ammonia are independent the oxygen uptake due to ammonia oxidation is 372-133 = 239 div. at R = 0. Taking the ammonia chemisorbed by the film as 71 div., the ratio of ammonia chemi-:sorbed: oxygen taken up due to oxidation is 71:239 i.e. 1:3.36 or approximately 3:10. 372.7

The products of oxidation of ammonia were sought by/

by examining the condensable matter present in the gas phase after illumination and also by washing the film with water and testing the washings for nitrate, nitrite, hydrazine and hydroxylamine by the following methods[39].

Nitrate. Aqueous extract + diphenylamine in conc. sulphuric acid gave no blue colour (quinoidal compound) indicating the absence of nitrate.

Limit of Identification 0.5×10^{-6} g.

Nitrite. Aqueous extract + Griess Llosvay reagent gave a pink colour indicating the presence of nitrite. The amount present was estimated as on page (41).

Hydrazine. Aqueous extract on filter paper, was exposed to salicylaldehyde vapour and examined under ultraviolet light. The absence of yellow fluorescence indicated that hydrazine was not present.

Limit of Identification 0.1×10^{-6} g.

Hydroxylamine. Aqueous extract + ammoniacal cupric ferricyanide did not give a white precipitate of cuprous ferricyanide indicating the absence of hydroxylamine.

Limit of Identification 0.2×10^{-6} g.

Water and carbon dioxide, in the gas phase, were the/

the only substances detected besides nitrite. The amounts of water and carbon dioxide obtained after each illumination in run 18 are shown below, and are ex-:pressed in divisions/hr., as the illuminations were for different lengths of time. Run 17 values are also shown.

TABLE 31

O_2 Treatment	H_2O Detected div/hr	CO_2 Detected div/hr	Time of Illumina-:tion hrs.	O_2 Uptake div.	H_2O in gas phase div.
1	0.067	0.155	82	84	5.4
2	0.045	0.051	167	91.3	7.6
3	0.150	0.097	70	46.1	10.5
Run 17	0.242	0.234	122	142	29.5

It can be seen from the above table, that after the first ammonia treatment (run 18) the rates of both water and carbon dioxide evolution on illumination in oxygen decreased considerably. After the second ammonia treatment the rates rose again, the rate of water evolution to a higher value than that observed in the first illumination. The high value for water in this case, together with the fact that the proportion of/

of water to carbon dioxide was higher after the second illumination than after the first is taken to indicate the production of water by oxidation of ammonia. The amounts of water and carbon dioxide found in the gas phase were small compared with the oxygen uptake as can be seen from the last column in table (31). Not all the water produced can be liberated into the gas phase, since a much higher rate of evolution of water during the second illumination would have resulted.

The nitrite present at the end of run 18c was estimated to be 4.24 μ moles NO_2^- (= 23.7 div.). This will represent the nitrite formed by oxidation of ammonia impurity in the zinc oxide (2.2 div. NO_2^- (see p. 80)), and nitrite formed by oxidation of ammonia chemisorbed during the ammonia treatments.

In run 17, the nitrite detected was 2.28 μ moles (= 12.7 div. NO_2^-) due to nitrite formed from impurity ammonia and nitrite formed from ammonia chemisorbed during ammonia treatment of the film.

As the film did not adsorb oxygen to completion during the first illumination in run 18, it seems likely, in view of the apparently independent natures of the photosorption of oxygen and the photo-oxidation of ammonia, that the photoadsorption of oxygen would continue in the later illuminations and affect the final extrapolated uptake. The total time of illumination of run 18 was 319 hrs. and another similar film which/

which was illuminated in oxygen continuously for 320 hrs. took up 80.3% of the extrapolated total oxygen uptake. If film 18 has behaved in this manner, the oxygen adsorbed will be 80.3% of 133 = 107 div. If this figure is subtracted from the total extrapolated uptake of 372 div., the oxygen taking part in oxidation becomes 265 div, and comparing this with the total amount of oxygen photosorbed (extrapolated from 18a) and the amount of ammonia chemisorbed, we have

265:133:71 = 3.74:1.87:1 or 3.98:2:1.07.

If the number of "oxygen sites" present on the surface is represented by the extrapolated oxygen uptake, and the number of "ammonia sites" is represented by the extrapolated dark uptake of ammonia, it would appear that twice as many oxygen sites exist as ammonia sites and that each adsorbed ammonia molecule is re-:sponsible for the removal of four oxygen molecules during illumination.

The amounts of nitrite which will be present when the oxidation is complete can be calculated if it is assumed that the amount formed is proportional to the oxygen taken up due to oxidation. In run 18 the total uptake (a + b + c) was 221.4 div. in 319 hrs. of which 107 div. can be attributed to oxygen photoadsorption leaving an uptake of114.9 div. due to oxidation of ammonia, the amount of nitrite formed being 23.7 - 2.2 = 21.5 div./

= 21.5 div. Thus with 265 div. uptake due to oxidation the nitrite formed would be 21.5 x 265/114.4 = 49.7 div. NO_2^-. Similarly, run 17 gives an infinity value of 43.2 div. NO_2^-.

During the second ammonia treatment in run 18, an uptake of 47.3 div. of ammonia was observed, being half (approximately) of the oxygen taken up in the second illumination (18b) (91.3 div). It would appear that this ammonia was not utilised in oxidation as no change in extrapolated oxygen uptake occurred on subsequent illumination (18c), although an increase in rate of uptake was observed.

ILLUMINATION OF AMMONIA TREATED ZINC OXIDE IN OXYGEN AND AMMONIA

A water bound film of 0.100 g. zinc oxide hyper-:fine in a type IV flask was given the usual evacuation and treated with ammonia at 25° C. as in run 17, and evacuated for a further 12 hours. Approx. 20 mm. of ammonia were admitted and allowed to come to equili-:brium (1 hr.), with the reaction space connected to a trap at room temperature. The trap was then immersed in liquid oxygen and the pressure change measured with the Bourdon Gauge as follows. The reaction space was isolated and air was removed from the gauge jacket until the gauge pointer neared the end of the scale. The tap from the reaction space was then opened for a very short time allowing ammonia to enter the cold trap and moving the pointer to the other end of the scale. This was repeated until all the gaseous and physically adsorbed ammonia had been removed and thus measured. Oxygen was now admitted to the cold trap and leads, and the cold trap was warmed to room temperature and time was allowed for diffusion of the ammonia into the oxygen. The mixture was then allowed to enter the reaction space and the system reached equilibrium in 1 hr. It was assumed that the same amount of ammonia had entered the reaction space during this time as that measured during freezing out.

The/

The reaction space was now sealed off and illumination commenced, a large pressure decrease being observed during 160 hours, at the end of which time illumination was discontinued. The gas phase was withdrawn through a cold trap in the usual way and the film then stood in contact with another cold trap overnight. The contents of the cold traps were identified and measured by the usual methods. The film was sealed off after overnight contact with the cold trap and a small pressure increase of 2 div. was observed during the next 24 hours. The gas evolved at this stage proved to be non-condensable and gave a red colour characteristic of nitrogen under electrical discharge.

From the contents of the cold trap the amounts of oxygen and ammonia which had reacted were calculated as follows. The total pressure decrease observed plus the amount of condensable matter collected in the gas phase other than ammonia represents the total pressure decrease due to the removal of oxygen and ammonia from the gas phase. The amount of ammonia collected in both cold traps is subtracted from the ammonia present initially to give the amount of ammonia "reacting". Thus the pressure decrease due to ammonia and oxygen, less the ammonia used in reaction gives the oxygen removed from the gas phase. The gaseous products/

products other than ammonia obtained in the cold traps were water, nitrous oxide and dinitrogen tetroxide. This calculation assumes (a) that the physically adsorbed ammonia remains essentially the same during the reaction, which will be essentially true for small changes in ammonia pressure, and (b) that no non-condensable gas e.g. nitrogen or hydrogen is produced during the oxidation.

The pressure and time readings taken are given in table (32) and are shown diagrammatically in figure (32A). Rate values derived from the experimental curve are given and rate curves are shown in figures (32B,C). The total pressure decreases of oxygen and ammonia are given in table (p.153) together with the products obtained.

TABLE 32/

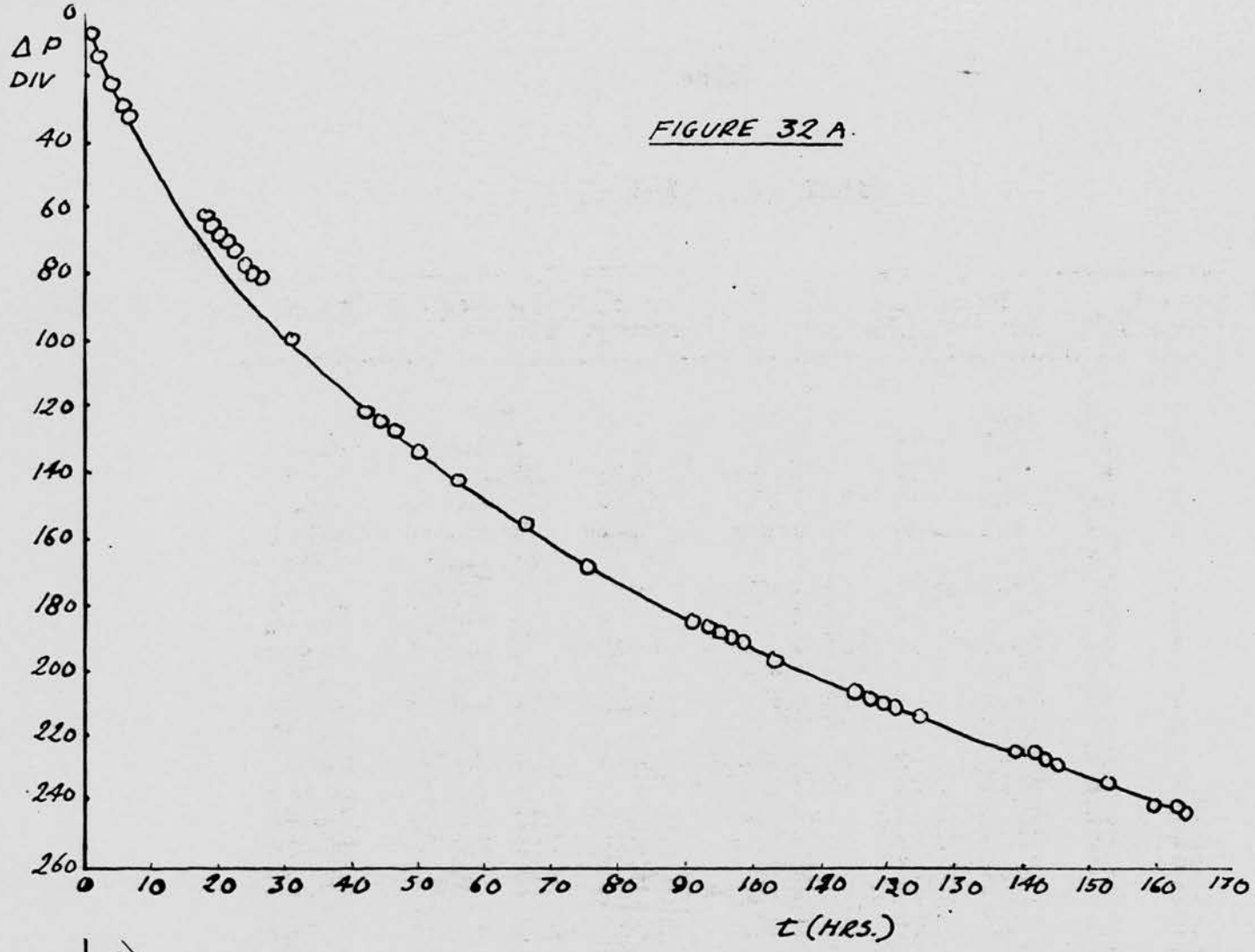


FIGURE 32 A

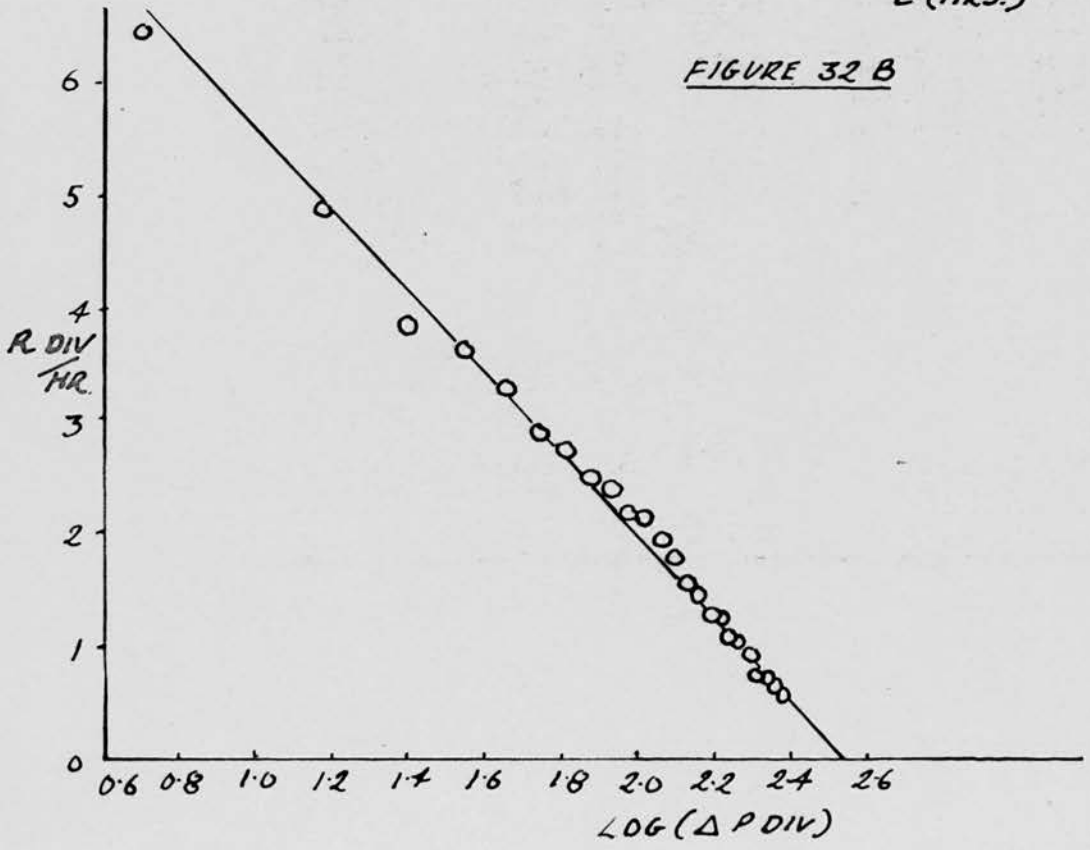


FIGURE 32 B

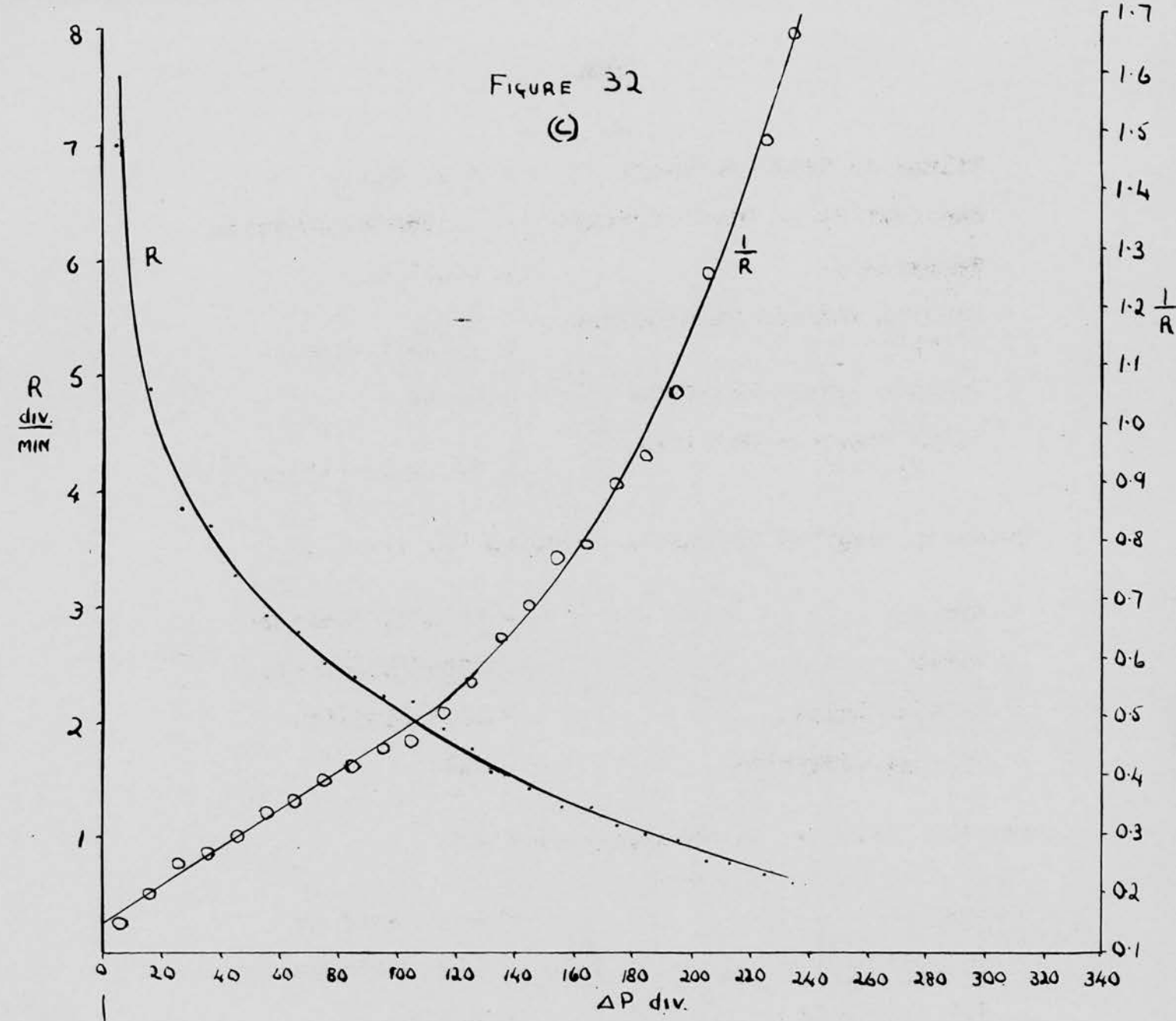
TABLE 32 RUN 19

t hr.	t min	ΔP div	t hr.	t min	ΣΔP div.	R div/hr	ΣΔP div	log ΣΔP	log R
0	00	0.0	66	10	155.7				
0	27	3.9	75	00	168.7	6.45	5	0.699	0.810
0	46	6.2	90	30	184.8	4.88	15	1.176	0.688
1	00	7.8	91	30	185.8	3.84	25	1.398	0.584
1	19	9.2	93	00	187.1	3.64	35	1.544	0.561
1	42	11.6	95	00	189.7	3.28	45	1.653	0.516
2	10	13.9	96	35	190.7	2.90	55	1.741	0.462
4	03	22.1	98	00	191.8	2.74	65	1.812	0.438
4	30	24.0	102	45	196.8	2.50	75	1.875	0.398
5	05	25.9	103	10	197.3	2.38	85	1.929	0.376
5	20	26.4	115	15	207.3	2.22	95	1.978	0.346
6	15	29.8	117	20	208.8	2.17	105	2.021	0.336
7	12	33.1	119	20	210.5	1.94	115	2.061	0.287
7	40	34.0	121	20	211.7	1.77	125	2.097	0.248
18	10	63.0	123	30	213.6	1.57	135	2.130	0.196
19	00	64.9	125	10	213.9	1.43	145	2.162	0.155
20	00	68.0	139	10	224.6	1.28	155	2.190	0.107
20	25	69.0	141	00	225.6	1.25	165	2.218	0.097
21	15	70.1	143	40	227.6	1.10	175	2.243	0.042
23	00	74.7	145	15	228.8	1.05	185	2.266	0.021
23	45	76.9	152	00	234.5	0.94	195	2.290	-0.028
24	10	77.1	162	20	241.7	0.79	205	2.312	-0.102
25	10	79.9	163	20	241.9	0.77	215	2.332	-0.114
26	07	81.5				0.67	225	2.352	-0.174
31	30	99.9				0.60	235	2.371	-0.222
31	50	99.9							
42	25	121.9							
43	05	122.2							
44	05	124.8							
45	50	127.8							
47	20	130.0							
48	30	131.8							
50	00	134.0							
56	20	142.7							

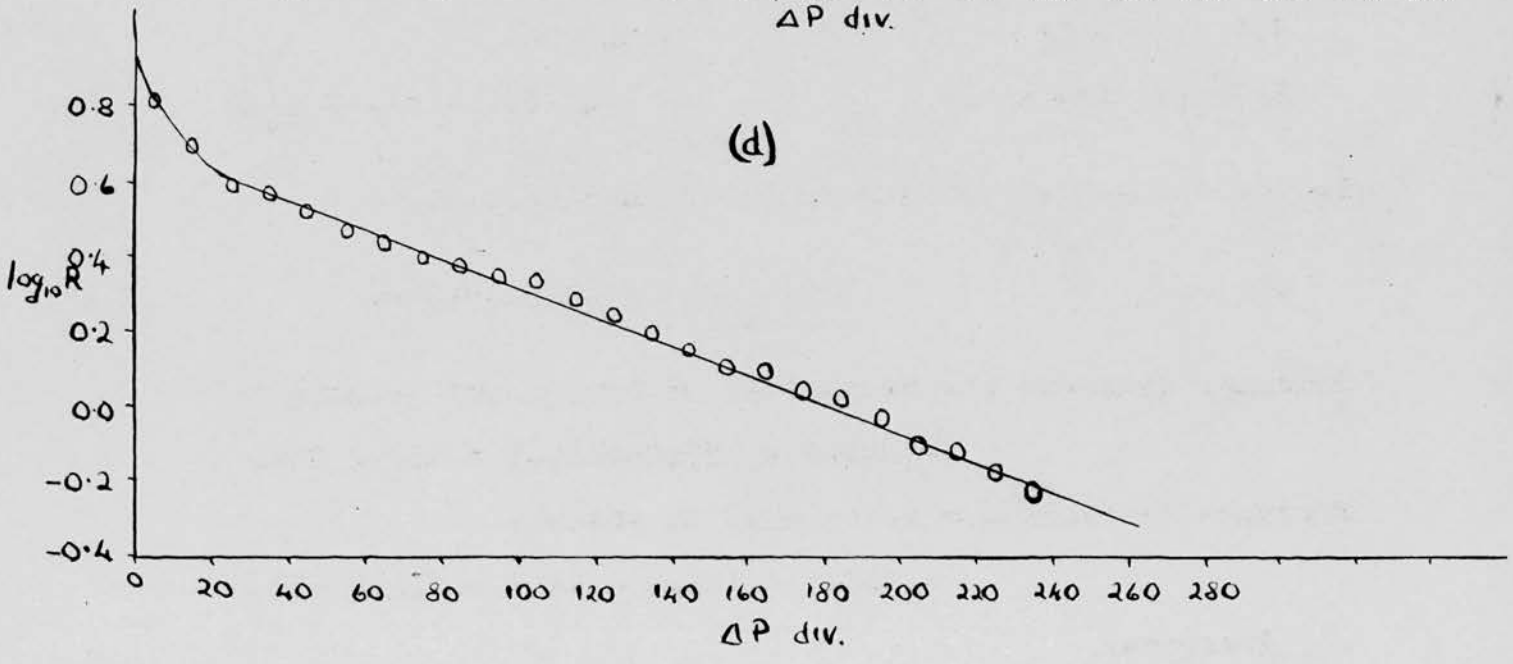
Volume/

FIGURE 32

(c)


R
1/R
R div./MIN
1/R
ΔP div.
0 20 40 40 80 100 120 140 160 180 200 220 240 260 280 300 320 340
1 2 3 4 5 6 7 8
0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7

(d)


log10R
ΔP div.
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280
-0.4 -0.2 0.0 0.2 0.4 0.6 0.8

Volume of Reaction Space	= 60.4 ml.
Sensitivity of Bourdon Gauge	= 0.0552 mm/division
Temperature	= 25.0° C.
Initial Ammonia in Reaction Space	= 340.8 divisions
Initial Oxygen Pressure	= 60 mm
Total Pressure decrease observed	= 241.9 divisions

Products obtained by rapidly pumping out gas phase

Ammonia	= 114.6 divisions
Water	= 159.0 divisions
Nitrous Oxide	= 12.5 divisions
Nitrogen Peroxide	= 0.0

Products obtained on standing overnight

Ammonia	= 14.8 divisions
Water	= 60.0 divisions
Nitrous Oxide	= 0.0
Nitrogen Peroxide	= 11.3 divisions N_2O_4

Products obtained by washing the film with water

Nitrite	= 22.8 divisions

Pressure decrease due to removal of Oxygen and Ammonia

= 241.9 + 159.0 + 12.5 = 413.4 div.

Pressure decrease due to removal of Ammonia

= 340.8 - 114.6 - 14.8 = 211.4 div.

∴ Pressure/

∴ Pressure decrease due to removal of Oxygen

= 413.4 - 211.4 = 202.0 div.

The dinitrogen tetroxide obtained was contaminated with a small amount of water. Another sample, obtained during a similar run, was dried over magnesium perchlorate and the following vapour pressures obtained at temperatures between -90° and -78°.

Temperature °C	Vapour Pressure (Experimental) mm (Hg)	Vapour Pressure (Calculated from International Critical Tables) mm (Hg)
-86.9°	0.0055	0.0091
-84.0°	0.0220	0.0155
-81.5°	0.0275	0.0240
-78.0°	0.0390	0.0427
-75.5°	0.0500	0.0661

The amount of water present in the dinitrogen tetroxide appeared to be small, the vapour pressure of the impure sample differing only slightly from that of the dehydrated sample, and thus no correction has been made for the water present.

It is noted that in the measurement of all condensable products, small errors, due to adsorption of the/

the gases on the walls of the apparatus, probably occur, particularly in the case of water vapour.

It would seem probable that the water detected was due largely to reaction between oxygen and ammonia and partly to desorption from the zinc oxide due to the slow ageing process (p. 64). A much larger amount of water was obtained on standing the above film (after illumina-:tion in oxygen and ammonia) in contact with a liquid oxygen cooled trap overnight than was detected, when a film which had been illuminated in oxygen or treated with ammonia, was allowed to stand in contact with a cold trap. In order to make a correction for water produced other than by photo-reaction of oxygen with ammonia, it was assumed that water was produced thermally, throughout the illumination and subsequent period in contact with the cold trap, at the same average rate as was observed during the last two dark ammonia treatments to which this film was subjected. The rate observed was 0.448 div./hr. i.e. 73.0 div. during the time of illumination of film (19).

The dinitrogen tetroxide was measured at 23° C. the total pressure being 22 div. (1.21 mm). The dissocia-:tion of this oxide(48) was calculated as 96% at 25° C. and a total pressure of 1.21 mm taking $K_{N_2O_4}$ as 0.1380, this being the value for the lowest pressure reported. The equivalent amount of N_2O_4 was 11.3 div. A correction/

correction of -2.2 div. has been made to the nitrite determination to allow for the nitrite formed due to impurities in the zinc oxide.

The reaction can be represented by the (unbalanced) equation:

202 div.O_2 + 211.4 div.NH_3 → 101.6 div.H_2O + 12.5 div. N_2O + 113 div. N_2O_4 + 22.8 div. NO_2^-, and an element balance can be made between reactants and products as follows:

	Reactants	Products	Reactants - Products
O	404.0	204.9	199.1
N	211.4	70.4	141.0
H	634.2	203.2	431.0

The ratio between the elements present in the reactants but not detected in the products is therefore

O : N : H = 199.1 : 141.0 : 431.0

= 1.41 : 1 : 3.05

A fresh film of 0.100 g. zinc oxide hyperfine was pre-:pared in a type I flask and after the usual evacuation was illuminated in 50 mm. of oxygen at 25° C. until 85% of the total extrapolated uptake of oxygen had occurred. The film was now treated with ammonia and the previous experiment was repeated, oxygen and ammonia being admitted and the products being measured in the same way./

way. The rates of pressure decrease were calculated and the plot of R against log $\Sigma\Delta P$ is shown in figure (33); the data are given in table (33). The amount of water liberated due to thermal desorption was calculated in the same way as before and the results are given in table (34). The units have been converted to those in the previous experiment to obtain a direct comparison between tables (p.153) and (34).

The amount of nitrite detected in this film was due to the illuminations described above and a subsequent illumination described on page (161) which was similar to the second illumination (O_2 + NH_3). The total nitrite was = 28.4 div. and making a correction of -2.2 div. for nitrite due to impurities in the film the nitrite due to the second illumination was calculated to be 17.2 div. on the assumption that equal amounts of nitrite would be produced during equal pressure decreases under illumination in oxygen-ammonia mixtures.

TABLE 33/

FIGURE 33

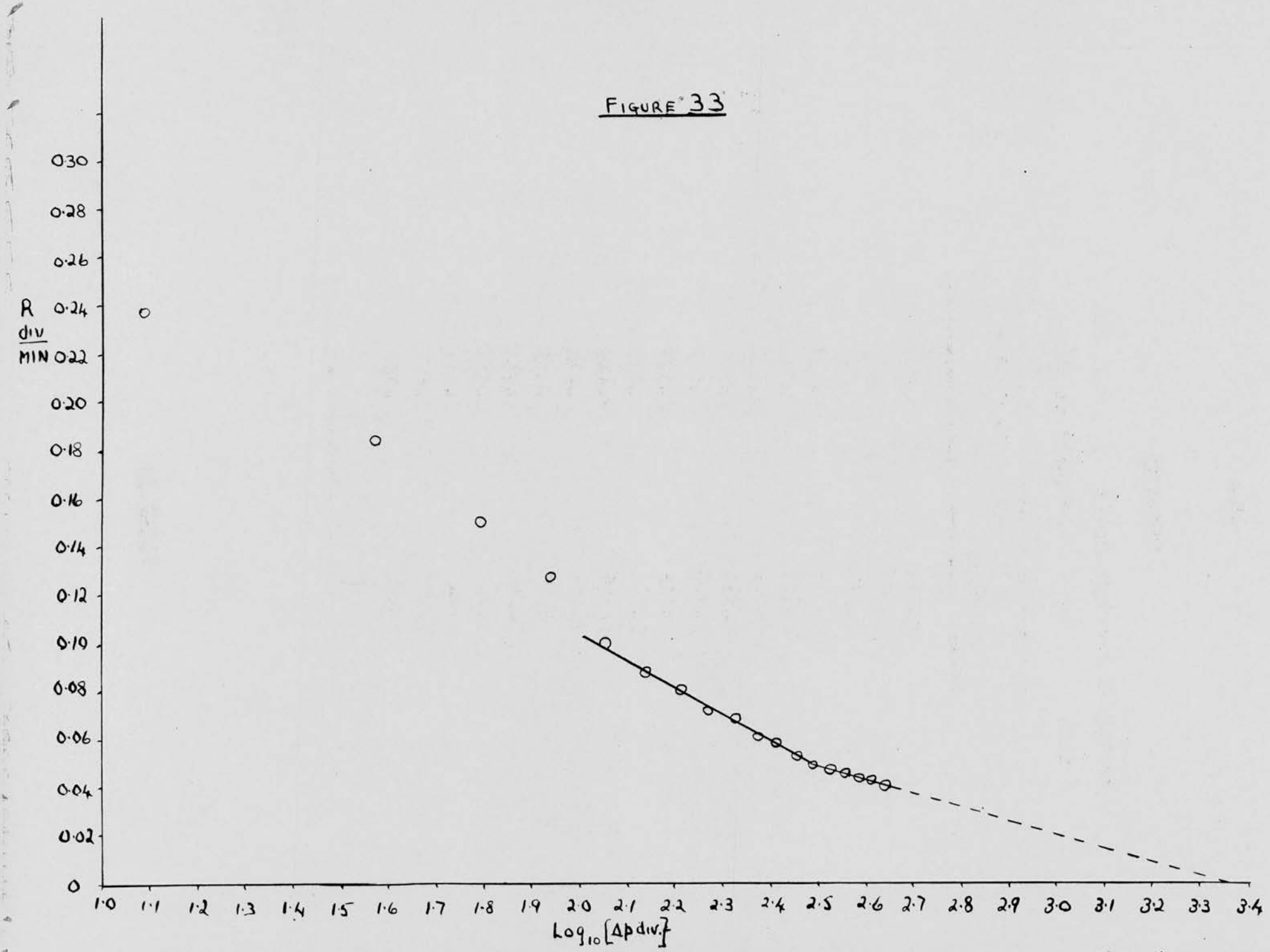

R div / MIN
0·30
0·28
0·26
0·24
0·22
0·20
0·18
0·16
0·14
0·12
0·10
0·08
0·06
0·04
0·02
0
1·0 1·1 1·2 1·3 1·4 1·5 1·6 1·7 1·8 1·9 2·0 2·1 2·2 2·3 2·4 2·5 2·6 2·7 2·8 2·9 3·0 3·1 3·2 3·3 3·4
Log10 [Δp div.]

TABLE 33

Volume of Reaction Space = 54.0 ml.

1 div. = 0.0303 mm (Hg).

R div/min	log $\Sigma\Delta$ P div
0.238	1.096
0.185	1.574
0.151	1.796
0.128	1.942
0.100	2.051
0.088	2.138
0.081	2.211
0.073	2.273
0.069	2.329
0.061	2.375
0.058	2.419
0.054	2.458
0.049	2.495
0.048	2.528
0.047	2.560
0.044	2.588
0.043	2.615
0.041	2.641

TABLE 34/

TABLE 34

1 div. in this table refers to 1 div. in 60.4 ml. with 1 div. = 0.0552 mm.

Initial Ammonia in Reaction Space	=	378.0 div.
Initial Oxygen Pressure	=	60 mm.
Total Pressure Decrease Observed	=	264 div.

Products obtained by rapidly pumping out gas phase

Ammonia	=	139.6
Water	=	120.6
Nitrous Oxide	=	26.5
Nitrogen Peroxide	=	0.0

Products obtained on standing overnight

Ammonia	=	33.8
Water	=	53.7
Nitrous Oxide	=	0.0
Nitrogen Peroxide	=	0.0

Products obtained by washing the film with water

Nitrite	=	17.2

Pressure decrease due to removal of Oxygen and Ammonia

= 264.0 + 147.1 = 411.1 div.

Pressure decrease due to removal of Ammonia

= 378.0 - 139.6 - 33.8 = 204.6 div.

Pressure/

Pressure decrease due to removal of Oxygen

$$= 411.1 - 204.6 = 216.5 \text{ div.}$$

The amount of water due to desorption during illumination and independent of the O_2 - NH_3 reaction was calculated to be 73.7 div.

A correction has been made for the nitrite formed due to oxidation of ammonia present as impurity (2.2 div. NO_2^- p. (80)).

This reaction can be represented as

$$216.5 \text{ div.} O_2 + 204.6 \text{ div.} NH_3 \rightarrow 100.7\ H_2O + 17.2\ NO_2^- + 26.5\ N_2O$$

and an element balance can be made between reactants and products as follows

Reactants		Products	Reactants - Products	
O	433	161.6	271.4	O
N	204.6	80.2	124.4	N
H	613.8	201.4	412.4	H

The ratio between the elements present in the reactants but not detected in the products is therefore

$$O : N : H = 271.4 : 124.4 : 412.4$$
$$= 2.18 : 1 : 3.31$$

Since the above results are calculated on the assumption that no non-condensable gas is produced on illumination, the following experiments were carried out based on the fact that titanium dioxide will, on illumination/

illumination, adsorb oxygen but not nitrogen or hydrogen.

After the experiment just described, 15.7 mm. Oxygen and 19.1 mm ammonia were admitted to the same film, which was then illuminated until a pressure decrease of some 100 div. had taken place. The gas phase was allowed to expand into a cold trap which was then closed, the remaining gases being pumped rapidly through another cold trap. The film was allowed to stand overnight in contact with a fresh cold trap. A film of 0.16 g. titanium dioxide was now attached to the bourdon gauge and evacuated for 24 hrs., having been previously evacuated for 5 days. The trap containing gases from the illumination was surrounded by liquid oxygen and (1) a small amount of the non-condensable gases were allowed to enter the reaction space. The titanium dioxide was now illuminated until the pressure remained steady for 10 hrs., the pressure decrease during illumination being less than that expected from complete adsorption. (2) A fresh sample of the non-condensable gases from the oxygen-ammonia illumination was now admitted to the reaction space and illumination was continued until a steady pressure was again reached. The residual gas was then allowed to come in contact with a cold trap at liquid oxygen temperature and was then pumped away. No condensable material was obtained. (3) A small amount of pure oxygen/

oxygen was now admitted to the film and illumination was again continued until a steady pressure was reached. The residual gas was again withdrawn through a liquid oxygen cooled trap, no condensable material being obtained. The results are given below.

1) Amount of gas admitted to T_iO_2 film = 11.8 div.
   Pressure decrease observed = 11.0 div.
   Gas not photosorbed = 0.8 div.

2) Amount of gas admitted to T_iO_2 film = 20.2 div.
   Pressure decrease observed = 19.1 div.
   Gas not photosorbed = 1.1 div.

3) Amount of oxygen admitted to T_iO_2 film = 14.4 div.
   Pressure decrease observed = 14.0 div.
   Gas not photosorbed = 0.4 div.

The gas not photoadsorbed in (3) (0.4 in 14.4) is taken as due to nitrogen in the cylinder oxygen, although Kennedy[6] has shown that when a fresh film of titanium dioxide is illuminated in vacuo, a small amount of a non-condensable gas is liberated at a constant rate, this process taking place also in small amounts of oxygen. If it is assumed that these factors operate in the above illuminations, which were all continued for the same length of time (24 hrs.), the amount of non-condensable gas formed in (1) and (2) above will have been 0.3 div. and 0.6 div. if (3) is due/

due to nitrogen impurity, or 0.4 div. if the gas in (3) is evolved from the film. Making these corrections we obtain the following values for the concentration of the non-condensable gas in the oxygen from the reaction space:-

in (1) 4.2% and 3.4%

in (2) 2.5% and 3.5%

It would thus appear that the latter correction is more important and that the concentration of non-condensable gas in the residual oxygen from the reaction space is between 3.4 and 3.5%.

Due to handling difficulties associated with sampling the non-condensable gases from the reaction space it was not possible to obtain an accurate measure of the condensable products present. It was assumed therefore that ratio of total pressure decrease; to oxygen taken up; to ammonia taken up; to products produced, was the same for both this illumination and the preceding one.

In this illumination the observed pressure decrease was 62.6 div. and the initial oxygen pressure was 15.7 mm (254.2 div. in the same units as experiment 19 i.e. reaction space volume = 60.4 ml. and gauge sensitivity = 0.0552 mm/div.)

The ratio of total pressure decrease: Oxygen uptake: Ammonia uptake in the first oxygen-ammonia illumination/

illumination in run 20 was 264 : 216.5 : 204.6, thus the second oxygen-ammonia illumination will give the ratio 62.6 : 51.4 : 48.5.

Thus oxygen remaining in gas phase after illumina-:tion = 254.2 - 51.4 = 202.8 div.

Thus the total amount of non-condensable gases other than oxygen remaining after this illumination was 3.4 to 3.5% of 202.8 = 7.2 to 7.3 div. or 14% of the oxygen uptake which will be in error by this amount. The ratio of the reactants in the first oxygen-ammonia illumination in run 20 must therefore be altered by increasing the oxygen uptake by 14.1%, when it becomes

$O_2 : NH_3 = 216.5 + 0.14 \times 216.5 : 204.6$

$= 247.1 : 216.5 \mp 1.21 : 1$

In the case of run 19 the ratio of $O_2 : NH_3$ becomes 230.5 : 211.4 = 1.09 : 1

The correction made above is small compared with the uptake of oxygen and ammonia.

It has been noted that a slow desorption of a non-condensable gas took place in long standing in vacuo after run (19). This behaviour has been observed with other films which have been illuminated in oxygen and ammonia, but not with films which have been treated with ammonia and subsequently illuminated in pure oxygen. The gas obtained in this way gave the characteristic red electric discharge for nitrogen but no/

no direct evidence as to its identity was obtained, the amount of gas obtained being very small.

If this gas is nitrogen it would seem probable that the non-condensable gas obtained in the final illumination in run (20) was also nitrogen. On this basis it is suggested that all, or at least most, of the undetected nitrogen in runs (19 and 20) is present as nitrogen gas and adsorbed nitrogen.

The similarity between runs (19) and (20) is taken to imply that the photo-sorption of oxygen does not take place during the oxidation of ammonia under these conditions.

The fall in rate of pressure decrease with time is seen from figure (33) to bear a linear relationship to log $\Sigma \Delta P$. Thus it is similar to the photo uptake of oxygen, and would appear to be a process involving the gradual filling of surface "electron traps". The only substance identified on the surface in these experiments was nitrite although dinitrogen tetroxide was found in small amount in film (19) on standing over a cold trap overnight.

The extrapolated value of $\Sigma \Delta P_\infty$ obtained from figure (33) is 2300 div. which represents the removal of 1889 div. O_2 and 1785 div. NH_3 from the gas phase and the formation of 184 div. NO_2^-. The extrapolated oxygen uptake for this film was 96 div. the ratio of nitrite/

nitrite adsorbed: oxygen sites (occupied) = 184:96 i.e. approx. 2:1.

It will be noted that a break occurs in the R against log $\Sigma\Delta P$ graph for run (20) while none occurs in the same graph for run (19). If the initial portion of these graphs are extrapolated, and the values obtained expressed in terms of oxygen uptake they are 249 div. in run (19) and 287 div. in run (20). The similarity of the figures would indicate that a break will also occur in the rate curve of this run[19], after a sufficiently large uptake has taken place, this being supported by the considerable degree of similarity between other features of the two runs.

DISCUSSION

DISCUSSION

From the experimental results, it has become clear that in all the photo-reactions investigated an unstable system is present when illumination is commenced, and that this system becomes increasingly stable with time, leading to a stable system after an infinite time of illumination. These systems involve active sites on the zinc oxide surface at which irreversible adsorption of various species occurs, a stable system resulting when all the sites are deactivated by adsorption. A definite number of sites exist in a film of zinc oxide with respect to a particular photo-reaction; different photo-reactions will not necessarily be associated with the same active sites.

A consideration of the rate curves reveals a marked difference between the uptakes of oxygen and nitric oxide; the latter shows an exponential type of uptake throughout illumination while the former exhibits an exponential type ($R \propto \Sigma \Delta P$) uptake only after a consider-:able uptake has taken place. The uptake of ammonia, on the other hand, takes place in the dark; and the uptake obeys a chemisorption type of rate curve ($\log R \propto \Sigma \Delta P$) while the photo-oxidation of ammonia appears to follow the same type of uptake curve as the photo-adsorption of oxygen.

The photo-uptake of oxygen, the photo-decomposition of/

of nitric oxide and the photo-oxidation of ammonia will now be considered in relation to one another and in relation to the course of these reactions on titanium dioxide, as investigated by Kennedy[6] and MacLean[7].

The Photo-Sorption of Oxygen

The rate of oxygen uptake on zinc oxide has been shown here to depend on the intensity of incident illumination, oxygen pressure, temperature and the amount of oxygen taken up. The dependence on the amount of oxygen taken up and hence on time was found to be initially approximately parabolic and finally approxi-:mately exponential, that is, the reciprocal rate of oxygen uptake bore a linear relationship to the amount of oxygen taken up over the first part of the uptake while the rate of uptake bore a linear relationship to the amount of oxygen taken up over the final part of the oxygen uptake. There appeared also to be a sharp transition from one type of uptake to the other.

When log R was plotted against $\Sigma \Delta P$, a broken straight line was obtained; the linear portions repre-:senting adsorption equations of the Roginsky-Zeldovich[37] type for chemisorption ($\Delta P = ae^{-bt}$, where a and b are constants). Taylor and Thon[38] have observed broken straight lines of this type for chemisorption on zinc oxide and have explained them in terms of surface heterogeneity.

The/

The break between the initial and final portions of the rate curves for the uptake of oxygen by zinc oxide would then appear to have a possible explanation in surface heterogeneity, and the final, exponential, portion can be taken to represent the uptake by one type of site only. If this is so it will be possible to obtain the rates of uptake due to these sites at various times during the initial part of the uptake and hence the rates of the other contributing processes. An example of the resolution of a rate curve in this way follows, taking run 1 as an example.

The equation of the exponential type of uptake is $(P - \Delta P) = e^{-(at - \ln P)}$ (1), where P is the value of ΔP at an infinite time, t = time and a is a constant; by differentiating with respect to t

$$\frac{d\,\Delta P}{dt} = ae^{-(at - \ln P)} \quad \ldots\ldots\ldots$$

$$\therefore \log R \left(= \frac{d\,\Delta P}{dt}\right) = \log a - \frac{a}{2.303} t + \log P \quad \ldots(2)$$

or by substitution $R = a(P - \Delta P)$ $\ldots(3)$

In the experimental section plots of R against $\Sigma\Delta P$ have been used to show the obedience of the uptake to equation (1). If we plot log R against t however, where t is the time corresponding to the $\Sigma\Delta P$ values in previous rate curves, we get a linear plot over that section of the uptake which obeys equation (1) and by drawing the linear portion back to t = o we obtain the rate curve for the exponential uptake under consideration.

The/

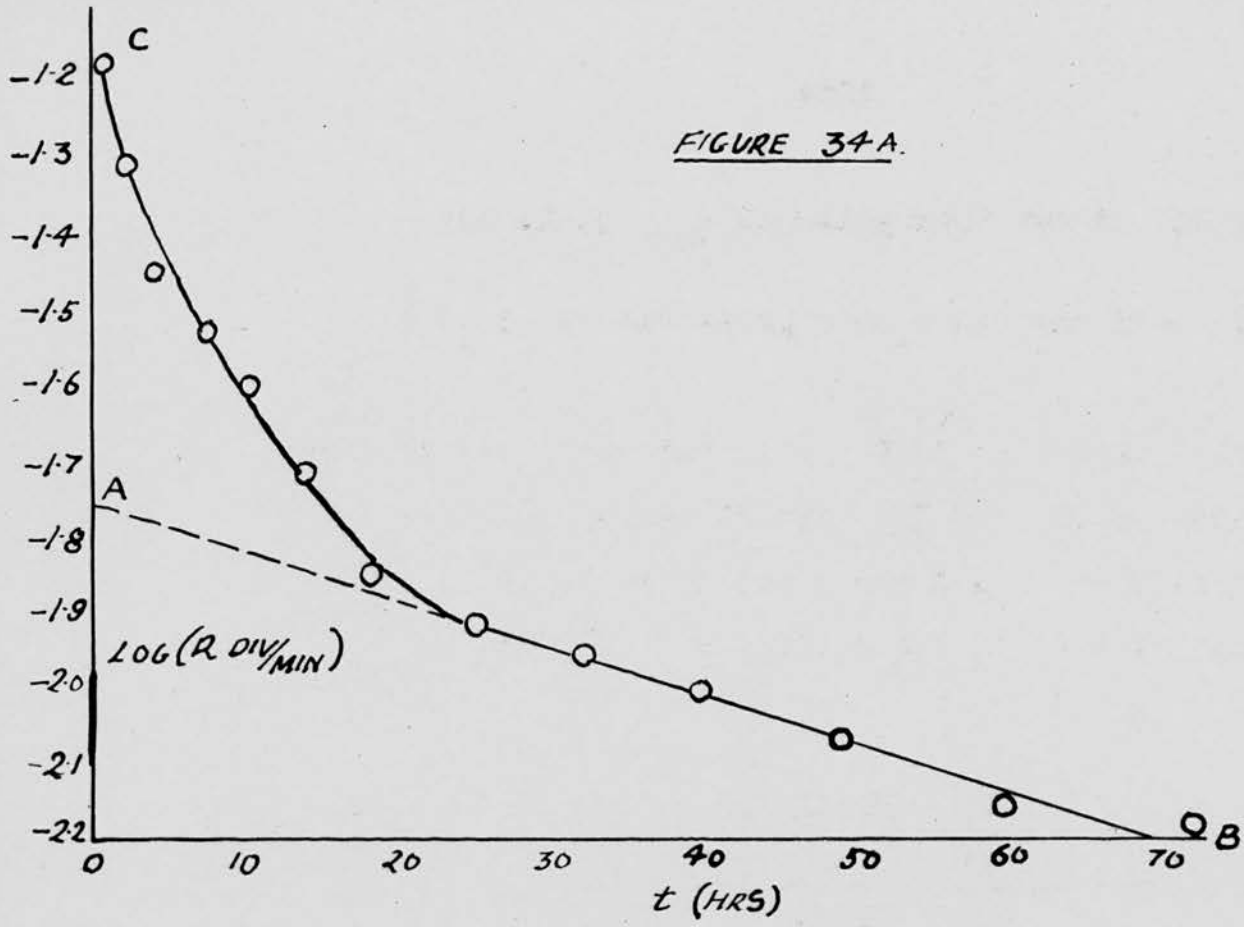


FIGURE 34A.

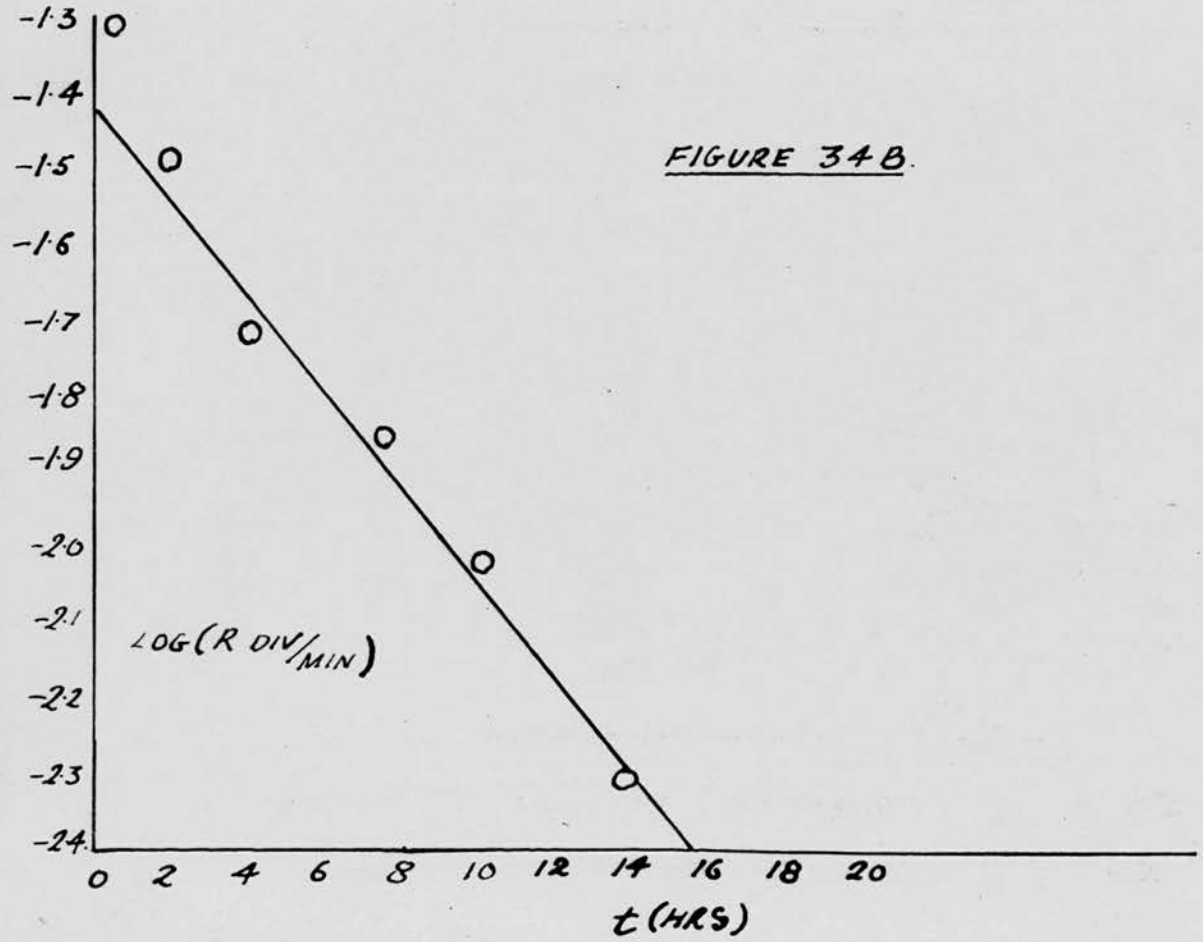


FIGURE 34B.

The gradient of the line gives us $\frac{a}{2.303}$ while the intercept with the log R axis gives the value of R_o (R at t = o).

From equation (2), $R_o = aP$ and hence the exponen-:tial equation (1) for this uptake can be written.

The data for log R and t are given in table (35) below and the plot of log R against t is shown in figure (34A).

TABLE 35

log R ($\frac{div}{min}$)	t hrs.
-1.18	0.55
-1.31	2.0
-1.45	4.1
-1.53	7.6
-1.60	10.1
-1.72	13.8
-1.85	18.0
-1.92	25.0
-1.96	32.0
-2.01	39.9
-2.07	49.0
-2.16	59.5
-2.18	71.9

From figure (34A) the gradient of line AB is 1.02 x 10^{-4} min^{-1} and log R_o is -1.764; thus a = 2.34 x 10^{-4} min^{-1}/

min^{-1} and R_o = 0.0172 div/min and hence P = 73.4 div.

As water and carbon dioxide were produced throughout illumination, the amount of oxygen taken up was 84 div. although the observed pressure decrease was 65.9 div. The rate values derived were thus too small by a factor of $\frac{84}{65.9}$ and thus the value of P derived above must be increased by this factor. The true value of P is thus 93.5 div., as against a value of 117 div. for the uptake of oxygen obtained by extrapolation of the plot of R against $\Sigma\Delta P$ a difference of 23.5 div. being apparent.

If we now examine the portion of the uptake not included in the exponential uptake described by the line AB in figure (34A), by means of the rates of uptake required to be added to those of line AB to give line CB we obtain, the rates in table (36) and the log R against t graph in figure (34B). Representing the rates of the two processes as R_1 and R_2, line CB gives log $(R_1 + R_2)$ while AB gives R_1 values only. The R_2 rates were thus found by $(R_1 + R_2) - R_1$.

TABLE 36

log $(R\frac{div.}{min.})$	t hr.
-1.303	0.55
-1.491	2.0
-1.717	4.1
-1.858	7.6
-2.022	10.1
-2.301	13.8
-3.097	18.0

It can be seen from figure (348) that a linear relationship exists between these log R values and t and a similar equation to that obtained above, can be derived for this uptake.

In this case P = 20.8 div. (corrected for gas phase water and carbon dioxide). The calculated uptake for processes other than the large exponential uptake was shown above to be 23.5 div., the difference between this value and P for this small exponential uptake being 2.7 div.

The following equation can be written for the two exponential uptakes

1) Large uptake $(93.5 - \Delta P) = e^{-(2.34 \times 10^{-4} t - 2.15)}$
   (t in mins.)
2) Small uptake $(20.8 - \Delta P) = e^{-(2.38 \times 10^{-3} t - 3.04)}$
   (t in mins.)

When the P values are calculated for run (2), the values obtained are:-

Large Uptake P = 80.8 div.

Small Uptake P = 21.6 div.

Total uptake = 102.4 div.

Total uptake obtained by extrapolating the R against $\Sigma\Delta P$ curve for the combined uptake = P = 100.0 div.

The difference here between experiment and calculation based on a resolution of the rate curve was -2.4 in this case. The agreement between experiment and calculation/

calculation would appear to be good in both runs.

It would therefore appear that the oxygen uptake curve is the result of two exponential type of curves with rate constants differing by a factor of 10. One way of interpreting this is to say that the oxygen uptake depends on the number of two sets of active sites which have different initial concentrations and different heats of adsorption.

Kennedy[6] has interpreted multiplicity of exponen-:tial curves due to differing intensities of illumina-:tion throughout the film. As the resolution of the uptake, in the case of zinc oxide yields only two exponential curves, it is considered unlikely that the variations of intensity of illumination are important in this case, as it would lead to a large number of exponential curves.

The relative rate method was employed using the later linear portion of the R against $\log \Sigma \Delta P$ curves and hence the dependence on the temperature, pressure and illumination is with respect to the larger exponen-:tial uptake.

From the dependence of rate on oxygen pressure we can infer that the oxygen is adsorbed as atoms in an initial fast reversible stage, as the Langmuir dissociative-adsorption isotherm is obeyed; the slow irreversible chemisorption of the atoms occurring subsequently.

A/

A charge transfer process between the oxygen and the zinc oxide is in agreement with the direct proportionality observed between the rate of uptake and the intensity of incident light.

In general the oxygen uptake by zinc oxide is kinetically the same as with titanium dioxide and can be related to the model proposed by Kennedy[6] for the photosorption of oxygen by titanium dioxide. In this scheme two types of surface sites are recognised with donation of electrons by the crystal to form chemisorbed O^-. The following scheme is given

(A) Reversible adsorption at A sites in accordance with a dissociation-adsorption type isotherm, with rapid equilibration

$$\tfrac{1}{2}\,O_2\ (\text{gas}) + A \rightleftharpoons (A^+ O^-)$$

(B) Chemisorption at sites B occur at 25° C. only on illumination within the fundamental absorption band and the number of B sites is normally much greater than A sites. A small fraction of the electrons in the conduction band becomes trapped at the A sites, freeing the chemisorbed O^- species for migration across the surface.

$$(A^+ O^-) + e \rightleftharpoons A + O^- \ (\text{rapid})$$

The number of migrating species is at any instant proportional to the number of electrons in the conduction band/

band and to the number of A sites occupied by oxygen. The chemisorbed oxygen thus freed migrates across the surface to the B sites to form the irreversibly chemisorbed species.

$$(A + O^-) + B \longrightarrow A + (B + O^-) \text{ slow}$$
$$(B + O^-) + \oplus \longrightarrow B^+ O^-$$

The rate determining step in this scheme is the migration of oxygen from A to B sites. The photo-:adsorption has been taken to show the same characteristics of adsorption as the $^{18}O_2 + {}^{16}O_2$ exchange reaction studied by Winter[12] for ZnO, A sites being identified with sites at which equilibrium may occur. These adsorption characteristics will certainly apply in the present case. No evidence of desorption of oxygen following interaction of ions with positive holes was obtained either for titanium dioxide or zinc oxide; on the other hand irreversibly adsorbed oxygen may be present as O^{2-} ions by further electron exchange.

In the present work, all the evidence is in accordance with a scheme of this type. The surface heterogeneity, however, can be included in the model and it is proposed that the above scheme be modified by the postulation of two types of either A or B sites; A sites if the rate is controlled by the $(A^+ O^-) + e \rightarrow A + O^-$ step and B sites if the migration from A to B sites is the rate determining factor. This would imply/

imply the existence of two processes differing only in activation energy and extent, more sites of one type A_1 or B_1 existing than of the other type A_2 or B_2. The difference in activation would presumably arise from geometric factors or from the existence of two types of photo-active centres of either type A or B, say Zn^+ and Zn^{++}.

The final step in the above scheme is irreversible chemisorption and it might be expected that the activation energy of the photo-uptake would be similar to that of dark chemisorption. Myasnikov[14] has obtained a figure of 8 - 9 kcals/mole for the chemi-:sorption of oxygen on zinc oxide from electroconduc-:tivity measurements which is similar to the experimental figure obtained here.

There is some doubt as to whether the trapping of positive holes, which will exist in the valence band in the case of illumination, can occur in the thermal case; thus it might be expected that the activation energy will apply to processes involving the A sites only. If the A site processes determine the reaction rate then no evidence has been obtained as to the final state of the irreversibly adsorbed oxygen as there is a possibility of recombination of atoms or ions to give molecular ions e.g. O_2^-.

While Kennedy has interpreted the initial portion of/

of the uptake curve for titanium dioxide as a parabola, the present author believes that the interpretation of this curve as the sum of two exponentials is more accurate in the case of zinc oxide.

The Evolution of Water and Carbon Dioxide

The main features of the evolution of water and carbon dioxide were,

1) A slow long term evolution in vacuo.
2) An ageing process so that an average rate of evolution was maintained with both continuous and intermittent pumping.
3) A very low pressure of these gases in contact with zinc oxide; when a film was allowed to stand in vacuo; no pressure rise greater than 0.1 mm occurred during several days standing.
4) An evolution into the gas phase in oxygen at 50 mm. at a slower rate to that obtained in vacuo with no illumination and at a higher rate in the case of carbon dioxide under illumination.
5) No evolution of water or carbon dioxide into the gas phase was observed in the presence of nitric oxide under illumination.
6) An evolution of water only in the presence of ammonia in the dark, at a rate slightly higher than that for evolution of water in vacuo.

The slow evolution of water and carbon dioxide suggests/

suggests the release of chemisorbed species, the slow ageing process also leading to this conclusion.

The presence of a small amount of water which cannot be removed by pumping at room temperature in a time of 30 hrs. has been detected on Mg O[38] and Al_2O_3[39], Fe_2O_3[40], SiO_2[40] and TiO_2[41], the surface oxide of the latter being completely converted into hydroxyl groups by contact with liquid water at room temperature. It would seem that this water can only be removed by pumping at elevated temperatures which depend on the oxide. Taylor and Sickman[42] found that water was adsorbed by zinc oxide almost instantaneously at room temperature with a heat of adsorption in the region of 30 kcals measured at temperatures in the region of 100°; they indicate that not all this water can be removed even by evacuation at 410°. Low and Taylor[43] have established that the rate of water adsorption at 100° C. follows the Elovich equation over the major part of the uptake.

The slow desorption of water and carbon dioxide together with the ageing process can be explained in terms of adsorbed species held at surface centres by means of charge transfer. The slow decay of these centres, by reversal of the charge transfer would give rise to physically adsorbed species which would exert a vapour pressure and could thus be removed completely from/

from the surface at a sufficiently low pressure.

In an atmosphere of oxygen, it is possible that a layer of physically adsorbed oxygen would upset the equilibrium of the physically adsorbed water and carbon dioxide and hence give rise to a greater concentration of these gases in the gas phase; a similar mechanism of desorption of water in the presence of ammonia is postulated i.e. the displacement of physically adsorbed water by physically adsorbed ammonia, the physically adsorbed water coming from ageing.

From the above it would appear that an equilibrium exists between chemisorbed and physically adsorbed water tending towards the physically adsorbed state in the case of water. No such desorption of chemisorbed ammonia was detected.

The increase in the desorption of carbon dioxide on illumination of zinc oxide in oxygen would indicate that an equilibrium between chemisorbed and physically adsorbed carbon dioxide is reached more rapidly under these conditions than in vacuo, the physically adsorbed carbon dioxide again being displaced by oxygen. It may be significant that, in many cases, equal amounts of water and carbon dioxide were found in the gas phase after illumination.

The/

The Photo-Decomposition of Nitric Oxide

When nitric oxide was allowed to come into contact with zinc oxide a slow pressure decrease was observed corresponding to a small dark uptake of nitric oxide, in the region of 2% of the total (extrapolated) uptake of oxygen. When the zinc oxide was then illuminated a much larger uptake of nitric oxide was observed, of the same order as the uptake of oxygen, and nitrous oxide was liberated in the proportion of NO : N_2O = 3:1. Nitrite was detected on the surface of the zinc oxide in the proportion of NO : NO_2^- = 3 : 1. The equation of the decomposition was therefore written as

$$e + 3\ NO \longrightarrow N_2O + NO_2^- \text{ (ads.)}$$

The uptake of nitric oxide was exponential with respect to time, the rate of uptake showing a linear relationship to ΔP and the equation of the uptake was therefore of the form $(P - \Delta P) = e^{-(at - \ln P)}$.

Although the dark uptake indicates surface heterogeneity, the photo-uptake is simpler than the oxygen uptake, and, as it is represented by a single exponential type of equation, it is of interest to compare it with the large exponential uptake of oxygen. As the initial stage of such an uptake will be the adsorption of nitric oxide and the overall surface process will be the adsorption of nitrite, it seems that the final extrapolated production of nitrite will

be the criterion for comparison with the oxygen uptake. The extrapolated final nitrite concentration, of a film of the same weight as that used in run (1) was 47 div. (in the same units as for run (1)) while the extra-:polated uptake of oxygen in run (1) was 93.5 div. for the large portion of the resolved uptake. The ratio of O_2 sites to NO_2^- sites is thus 93.5 : 47.0 or approximately 2 : 1; thus there are half as many nitrite sites as oxygen sites if the oxygen sites are taken to each contain an oxygen molecule or after deactivation.

In the case of titanium dioxide, MacLean[7] has shown that there are twice as many nitrite sites as oxygen sites on the above basis, which would indicate a marked difference between zinc oxide and titanium dioxide in this respect. The fact that the kinetics of the oxygen uptakes of the two oxides are so similar might be taken to argue that the same proportion of nitrite sites to oxygen sites would exist in them if the same surface centres were involved in both adsorp-:tions. The fact that this does not apply and that intermediate treatment with nitric oxide does not affect the oxygen uptake by zinc oxide would point to the existence of separate sites, while the fact that nitric oxide uptake on zinc oxide is affected by previous illumination in oxygen, and the mutual interference of nitric oxide and oxygen uptakes on titanium dioxide[6], indicate/

indicate a connection between the surface sites.

The mechanism of the decomposition can be repre-:sented in terms of the A and B sites for the oxygen uptake without any reference to heterogeneity of either A or B sites in this case. The scheme of Kennedy can be modified in detail to explain the observed reaction, the electronic mechanism being unaltered. This scheme is as follows. The initial adsorption is written as

$$2\,NO + A \rightleftharpoons A^+ NO_2^- + N$$

the NO_2^- is considered to be free to migrate by light action,

$$A^+ NO_2^- + N + e \longrightarrow A + N + NO_2^-$$

migration then leads to irreversible adsorption,

$$B + NO_2^- + \oplus \longrightarrow B^+ NO_2^-$$

The production of N_2O is represented by

$$NO + N \longrightarrow N_2O$$

This satisfies the overall equation in the case of zinc oxide, while the overall equation of

$$4\,NO \longrightarrow N_2O + N_2O_3\ (ads.)$$

for titanium dioxide is satisfied by the final step

$$B^+ NO_2^- + NO \longrightarrow B^+ N_2O_3^-$$

MacLean[7] has obtained fresh results for titanium dioxide detecting a slow desorption of nitrous oxide after illumination was ceased and estimating surface nitrite, which leads to the same equation, as was obtained in this work.

As/

As Kennedy points out, the migrating species may be O^- implying that the dark adsorption of NO to give NO_2^- or $N_2O_3^-$ would be greater on a sample of oxide previously illuminated in oxygen. It would seem also that this would give rise to the same number of "nitrite sites" as oxygen sites which was not observed.

In general, it would appear that although a similar mechanism of decomposition exists for both zinc oxide and titanium dioxide, differences in surface conditions lead to differences in the proportion of nitrite sites to oxygen sites.

Due to the slow rate of uptake of nitric oxide, it was not possible to apply the relative rate method with sufficient accuracy, to investigate the pressure dependence of the uptake.

Dark Uptake and Photo-Oxidation of Ammonia

The dark uptake of ammonia was of two types, a reversible rapid adsorption of ammonia and a slower irreversible process. The overall rate of uptake obeyed a Roginsky-Zeldovich type of equation and it seems likely that the irreversible uptake is due to chemisorption, with charge transfer at surface sites. A limiting value for the irreversible adsorption was apparent and a value of 71 div. (in the units used in the previous part of the discussion) was obtained, which/

which cannot be correlated with either oxygen or nitrite adsorption in terms of number of sites.

The chemisorption of ammonia on zinc oxide was shown to lead to an enhanced uptake on subsequent illumination in oxygen with the production of NO_2^- on the surface. This oxidation of ammonia did not lead to any stoichiometric relationship between reactants and products; it was possible, however, to relate the reactants in the ratio of $NH_3 : O_2 = 1 : 4$ by extra-:polation of an R against log $\Sigma \Delta P$ curve. This curve showed a break in the same way as oxygen photosorption and the same type of resolution of the R against t curve was used as in the case of oxygen photo-adsorption. In run 18 the film was illuminated in oxygen initially, then treated with ammonia and subsequently illuminated in oxygen. This second illumination is being considered here and the log rates were plotted against the time from the start of this illumination. The resolution gave similar results to that for oxygen uptake two exponential portions being identified and P values obtained. The initial rate value at 2 hrs. was high in this case. The P values obtained were 188 and 25.4 div.; the (a) constants being 4.52×10^{-5} and 7.68×10^{-3} respectively. It has been taken that the P values represent the reaction due to oxidation of ammonia and a surface heterogeneity is apparent which

can/

can be compared with that found for the oxygen photo-:adsorption. A comparison of the P constants between oxygen uptake due to photosorption and due to photo-oxidation (p. 142) can thus be made. Using P_1 and P_2 to distinguish the large and small components of the uptake.

Photoadsorption $P_1 = 93.5$; $P_2 = 20.8$ div.
Oxidation of Ammonia $P_1 = 188$; $P_2 = 25.4$ div.

It is at once apparent that while the value of P_1 for oxidation is twice that for photosorption, the P_2 values are similar in the two cases. The sum of P_1 and P_2 for oxidation is 213.9 div. while the value for the total (extrap.) uptake of oxygen due to ammonia oxidation was 265 from R against log $\Sigma \Delta P$ plots. It is considered that the resolution of the rate curves into single exponential type curves gives a more accurate method of obtaining P values and the above P values are preferred to the total P value from the log plot.

In view of the new P values obtained, the ratio of reactants must be changed to $NH_3 : O_2 = 71 : 213.4$ = 1 : 3 (approx.) overall.

Using the value of 213.4 for the total amount of oxygen taken up due to 71 div. of adsorbed ammonia, it would appear that the total nitrite produced by this oxygen/

oxygen would be 21.5 x $\frac{213.4}{114.4}$ = 40.1 div. the other extrapolated value of 265 div. giving a value of 43.2 div. nitrite.

The proportion of nitrite produced to oxygen taken up is $\frac{21.5}{114.4} = \frac{1}{5.32}$.

The apparent independence of photo-sorption of oxygen and photo-oxidation of ammonia would indicate a difference in sites for the two reactions. The ratios of P_1 and P_2 values above however show a simple relation-:ship between the numbers of sites the figures represent for photosorption and oxidation, the relationship being different in the case of P_1 and P_2 however.

Although it has been established that oxidation of ammonia in this way leads to the formation of nitrite, not all the nitrogen present can be accounted for in this way. The mechanism of this oxidation cannot therefore be elucidated on the information obtained although there would appear to be a surface process of the same type as for the photosorption of oxygen which probably includes charge transfer with the solid leading to the formation of irreversibly adsorbed species. In both photo-adsorption and oxidation of ammonia, it would appear that the final state is one of surface deactivation by chemisorption.

With titanium dioxide[7] the adsorption of ammonia and/

and its subsequent oxidation involve different ratios of both overall P values as compared with oxygen photo-:adsorption, and reactants. The dark uptake of ammonia was found to be four times as great as the total photoadsorption of oxygen while the reactants in the subsequent oxidation were in the ratio $NH_3 : O_2 = 4 : 6$. Nitrite was detected on the surface after illumination but only in trace quantities.

Oxidation of Ammonia at High Partial Pressure

When a film of zinc oxide, which had been treated with ammonia in the dark, was illuminated in presence of oxygen and ammonia, a large decrease in pressure occurred, which was represented by a linear R against log $\Sigma\Delta$ P curve, a break occurring as in the case of illumination in oxygen. The illumination of the film in oxygen previous to this treatment, did not affect the uptakes of oxygen and ammonia.

The products were: water, nitrous oxide, dinitrogen tetroxide and nitrite in the case of a film not pre-:viously illuminated in oxygen and water, nitrous oxide and nitrite in the case of a film which was previously illuminated in oxygen.

The uptake curve was resolved into two exponential type curves, as was described previously, two P values being obtained, which were P_1 = 944 div. and P_2 = 94.2 div. giving/

giving a total extrapolated value of 1038.2 div. The R against log $\leq \Delta P$ plots gives a value of 2300 div. It is clear that in this case where a very large uptake has taken place, that no relation exists between these two methods of extrapolation. It is intended to accept the extrapolation obtained by resolution of the exponential type of uptake curve, in discussing relative uptakes with respect to uptake of oxygen and nitric oxide. The reason for this is the uniform way in which uptakes of different gases give two exponential type plots on resolution of their rate curves; although some doubt must exist as to whether this is the correct procedure.

The amounts of oxygen and ammonia represented by the P values above are

P_1 NH_3 = 731 divs. O_2 = 774 divs.
P_2 NH_3 = 73.0 divs. O_2 = 77.2 divs.

assuming the uptake of each to be proportional to the pressure change occurring, and the amount of nitrite formed by the oxidation will be 75.5 and 7.53 div. corresponding to the P_1 and P_2 values above, or a total of 83.0 div.

As was noted in the experimental section, not all of the reactants were accounted for in the products and an element balance gave the proportions of the elements not accounted for. It was also noted that a non-condensable/

condensable gas was detected in the gas phase to an extent of 14% of the observed oxygen uptake. The balance of elements not detected in the products was as follows for runs 19 and 20, taking the non-condensable gas into account but not assigning any identity to it.

Run 19 O : N : H = 255.6 : 141.0 : 431.0

= 1.81 : 1 : 3.05

N : non-condensable gas = 1 : 0.40

Run 20 O : N : H = 332.0 : 124.4 : 412.4

= 2.67 : 1 : 3.31

N : non-condensable gas = 1 : 0.49

A difference in these ratios is apparent and a comparison of the products gives the following results

Run 19 H_2O : N_2O : N_2O_4 : NO_2^- = 101.6:12.5:11.3:22.8 div.

Run 20 H_2O : N_2O : N_2O_4 : NO_2^- = 100.7:26.5:0.0:17.2 div.

It can be seen that different amounts of products were obtained with an oxygen pretreated film run 20 and an untreated film run 19. Film 19 which received no pretreatment with oxygen appears to have yielded a greater proportion of oxygen rich products, N_2O_4 and NO_2^- than film 20.

The non-condensable gas may have been either nitrogen or hydrogen. The nitrogen alternative would appear to be more likely in view of the variety of oxidised/

oxidised forms obtained, and the slow desorption of a non-condensable gas from the film after illumination had ceased, might lead to the conclusion that all the nitrogen unaccounted for, was present as nitrogen gas and adsorbed nitrogen, although MacLean[7] who has also observed the evolution of a non-condensable gas in this way has ascribed its production to a slow decomposition of adsorbed species, particularly azoic acid.

A general approach to these results can be made, in terms of varying degrees of oxidation of adsorbed ammonia most of the products leaving the surface or being loosely held to it.

The limiting stage in the reaction would appear to be the irreversible adsorption of one or more species causing deactivation of the surface; nitrite was the only adsorbed material detected after oxidation of ammonia had taken place.

While no stoichiometric equation can be written to include the reactants and products, a relationship exists between the amounts of ammonia and oxygen reacting, which is approximately 1:1 for both films. MacLean[7] has shown that with titanium dioxide, this ratio of reactants is approximately 3:2 for oxygen to ammonia and has obtained the same condensable products, with the exception of dinitrogen tetroxide, as in the

case/

case of zinc oxide, although in different proportions: some nitrite was also detected.

Rao[46] has investigated the photo-oxidation of ammonia in aqueous solution in contact with titanium dioxide and proposed a mechanism leading to reduction of the oxide to T_iO with production of hydroxylamine and subsequent oxidation of hydroxylamine to nitrite

$$T_iO_2^* + NH_3 \longrightarrow T_iO + NH_2OH$$
$$NH_2OH + O_2 \longrightarrow HNO_2 + H_2O.$$

Griessboch and Reinhardt,[47] investigating the catalytic oxidation of ammonia on a $Co_3O_4 - Al_2O_3$ catalyst, have proposed $NH_3 \longrightarrow NH$ or NH_2 as the first step with subsequent oxidation to nitric oxide, in a two step process.

$$NH_3 \longrightarrow NH_2 + H$$
$$NH_2 + O_2 \longrightarrow NO + H_2O$$

If nitric oxide were produced in the presence of illuminated zinc oxide, the production of nitrite and nitrous oxide could be expected. A scheme of the latter type is envisaged as taking place in the present work, with possibly the production of nitrite also from hydroxylamine formed as in the former scheme. Any nitrogen formed may have resulted from

$$NH_2 + \tfrac{1}{2} O_2 \longrightarrow \tfrac{1}{2} N_2 + H_2O$$

another possibility for nitrite formation being

$$NH_3 \longrightarrow NH + H_2$$
$$2\ NH + \tfrac{1}{2} O_2 \longrightarrow \tfrac{1}{2} N_2 + H_2O$$

the/

the initial step leading to hydrogen formation, which may be present in the reaction mixture after illumination as part or all of the non-condensable products.

The oxygen and hydrogen not accounted for must remain adsorbed, possibly as H_2O, OH and/or as part of a nitrogen containing complex.

The formation of N_2O_4 by $2NO + O_2 \longrightarrow N_2O_4$ would appear to be the most likely mechanism and this may be a surface or gas phase process.

General Discussion

The uptake of oxygen, decomposition of nitric oxide and oxidation of ammonia, all show exponential behaviour with respect to time; the uptakes being apparently the resultants of two exponential uptakes in the cases of oxygen photoadsorption. A comparison can be made of the uptakes of oxygen and the chemisorption of nitrite for the reactions studied, using values extrapolated from the resolved R against $\Sigma\Delta P$ plots, and these P values can be related to the comparative numbers of active sites present on the surface .

Oxygen Sites: Extrapolated uptakes in arbitary units (divs.)

	Slow Uptake	Fast Uptake
For Photoadsorption on Untreated Film =	93.5	20.8

Photoadsorption/

	Slow Uptake	Fast Uptake
Photoadsorption on Ammonia Treated Film (due to oxidation)	= 188	25.4

Nitrite Sites: Calculated from amount formed during uptake of a known amount of oxygen.

NO_2^- from Oxidation of Chemisorbed Ammonia	43.2
NO_2^- from Oxidation of Ammonia with gas phase ammonia	83.0
NO_2^- from Decomposition of Nitric Oxide	47

No evidence of the heterogeneity or otherwise of nitrite sites could be obtained by the method employed in the ammonia experiments.

A comparison of nitrite sites show almost equal numbers for oxidation of chemisorbed ammonia and the decomposition of nitric oxide, but almost twice this number is obtained on oxidation of ammonia in the presence of gaseous ammonia. It would also appear that the number of nitrite sites is half the number of sites for photoadsorption of oxygen.

In general the presence of ammonia considerably modifies the oxygen uptake and apparently modifies the surface, more oxygen being taken up in the presence of chemisorbed ammonia than can be reasonably accounted for by oxidation.

When ammonia is present in the gas phase, however, it/

it would appear that oxidation of ammonia is the only oxygen consuming process.

Considerable differences are apparent in the oxidation of ammonia on zinc oxide and titanium dioxide, which might be expected from structural differences in the oxides. It is surprising in view of these differences that such similar behaviour is observed in the case of photo-adsorption of oxygen, and it is to be expected that other oxides and probably sulphides will show photoadsorption of oxygen under suitable conditions.

The studies of the photo-reactions of zinc oxide in this work have indicated extensive surface hetero-:geneity and the deactivation of the surface by irreversible chemisorption of a variety of species, these phenomena being closely linked to electron availability at the surface.

SUMMARY

An irreversible uptake of oxygen occurred when films of zinc oxide were illuminated at 25° C. with light within the fundamental absorption band of the solid. The rate of uptake was found to be a function of oxygen pressure; intensity of light, temperature and the amount of oxygen taken up. The rate was directly proportional to the rate of reversibly adsorbed oxygen atoms on the surface, and to the intensity of incident light; an apparent activation energy was calculated; an approximately parabolic law was obeyed in the initial stages of the uptake and an exponential law in the final stages; it was found that the total uptake could be represented as the resultant of two exponential type uptakes with different rate constants.

The uptake of oxygen was accompanied by the evolution of water and carbon dioxide which had remained chemisorbed on the film during preliminary evacuation.

Illumination of zinc oxide in nitric oxide resulted in an uptake of nitric oxide with the production of nitrous oxide and nitrite in accordance with the equation

$$3\ NO\ (gas) + e \xrightarrow{h\upsilon} N_2O\ (gas) + NO_2^-\ (ads.)$$

This/

This uptake obeyed an exponential law.

The oxidation of ammonia chemisorbed by zinc oxide was investigated in the presence of gaseous oxygen and gaseous oxygen-ammonia mixture. Evidence of a complex mechanism, which could not be fully elucidated, was found. The kinetics of the oxidation appeared to be similar to those of oxygen uptake.

Discussion is given of the relationship of the photo-reactions studied to the electronic and surface structure of zinc oxide, and to the results of analagous work on titanium dioxide.

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